Excited- and Ground-State Versions of the Tri-π-methane Rearrangement: Mechanistic and Exploratory Organic Photochemistry[1]

Howard E. Zimmerman* and Vladimír Církva

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 bonded to a single carbon leading to π-substituted cyclopropanes is now well established. The present research had as its goal the exploration of molecular systems having three π-moieties attached to an sp^3-hybridized atom in a search for a tri-π-methane rearrangement. Indeed, it was found that such systems do rearrange photochemically to afford cyclopentenes. However, it was also established that vinylcyclopropanes ring-expand to cyclopentenes on direct irradiation. Since both three-ring and five-ring photoproducts often are found to be produced, it was important to establish that the observed photochemistry was really the result of a true single-step tri-π-methane rearrangement and not the consequence of two sequential rearrangements, first to form a vinyl cyclopropane which subsequently ring expanded to the cyclopentene. The general situation has three species—A, B, and C—corresponding to tri-π-methane reactant A, vinylcyclopropane photoproduct B, and cyclopentene photoproduct C. Three rate constants are involved, k_1 for A → B, k_2 for A → C, and k_3 for B → C. The kinetics were applied to two examples with provision to avoid differential light absorption; this utilized singlet sensitization. It was determined that direct formation of the cyclopentene photoproduct proceeds more rapidly than the ring-expansion route. In contrast to the di-π-methane rearrangement, the tri-π-methane reaction was found to be preferred by the singlet, while in these sterically congested systems, the triplet led to di-π-methane reactivity. Finally, a ground-state counterpart of the reaction was obtained.

Introduction

Organic photochemistry has two main directions. One is research aimed at discovering new photochemical reactions, mechanisms, and theory, while the other involves the study of the photophysics of known processes. The present study was initiated with the first direction in mind. It began with the knowledge that the di-π-methane rearrangement had been rather thoroughly studied and was well understood.[2] This posed the question of whether a counterpart tri-π-methane process was attainable. Previously, we had observed one example in a solid-state process,[5] but a failure of a tri-π-methane process in the case of solution photochemistry.[6] Thus, the search for a tri-π-methane rearrangement reaction in solution presented a special challenge.

Results

Synthetic Aspects. Our investigation began with the synthesis of a number of tri-π-methane reactants. Scheme 1 presents a convenient route to tris-diphenylvinylmethanes. There were several known syntheses[7] of the parent tris-diphenylvinylmethane **3**, but we devised the one in Scheme 1, which proved simplest. This combined two known types of reactions. Thus, the formation of **3** involves an initial Prins reaction of **1** and **2**, anticipated to lead first to carbinol **7** (Scheme 2). This is in analogy with the reaction of benzaldehyde with diphenylethylene.[8] Under the acidic conditions, this carbinol was known[9] to react with diphenylethylene to afford the desired **3**.

(1) This is paper 260 of our general series. For paper 259, see: Zimmerman, H. E.; Církva, V.; Jiang, L. *Tetrahedron Lett.* **2000**, *41*, 9595−9597.

(2) The mechanism of the rearrangement was first reported in 1967 in the transformation of barrelene[3a] to semi-bullvalene.[4] Although barrelene had been synthesized earlier[3a,b] and the rearrangement observed,[3b] the first mechanism given was not correct. The correct mechanism was elucidated in 1967.[3c] Additionally, we note that in the correct mechanism, one can construe fifty percent of the semibullvalene product as arriving from a Tri-π-methane mechanism. The case, however, is somewhat artificial since the two ends of the allylic system of "diradical II" are symmetrically disposed to the remaining one-electron center.

(3) (a) Zimmerman, H. E.; Paufler, R. *J. Am. Chem. Soc.* **1960**, *82*, 1514−1515. (b) Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183−184. (c) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932−3933. For a recent review see Zimmerman, H. E.; Armesto, D. *Chem. Rev.* **1996**, *96*, 3065−3112.

(4) (a) See ref 3c. (b) Zimmerman, H. E.; Iwamura, H. *J. Am. Chem. Soc.* **1968**, *90*, 4763−4764. (c) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A.; Grunewald, G. L. *J. Am. Chem. Soc.* **1969**, *91*, 3316−3323. (d) Zimmerman, H. E.; Robbins, J. D.; Schantl, J. *J. Am. Chem. Soc.* **1969**, *91*, 5878−5879. (e) Zimmerman, H. E.; Iwamura, H. *J. Am. Chem. Soc.* **1970**, *92*, 2015−2022.

(5) (a) Zimmerman, H. E.; Zuraw, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 7974−7989. (b) For a reaction which may be termed a tri-π-methane rearrangement in utilizing three π-bonds in a different way, see: Pokkuluri, P. R.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1990**, *112*, 3676−3677.

(6) (a) Mong, G. M.S. Thesis, University of Wisconsin—Madison, 1979. (b) Modification of the procedure of Mong, G.[6a]

(7) (a) Wittig, G.; Kosack, H. *Justus Liebigs Ann. Chem.* **1937**, *529*, 167−184. (b) Höft, E.; Gründemann, E.; Gross, H. *Liebigs Ann. Chem.* **1969**, *722*, 225−227.

(8) (a) Jones, D. W. J. *Chem. Soc. C* **1966**, 1026−1028. (b) McEwen, W. E.; Yee, T. T.; Liao, T.-K.; Wolf, A. P. *J. Org. Chem.* **1967**, *32*, 1947−1954.

(9) Cheminat, B.; Guillaumet, G.; Rambaud, R. *Bull. Soc. Chim. Fr.* **1972**, 3422−3426.

10.1021/jo001601b

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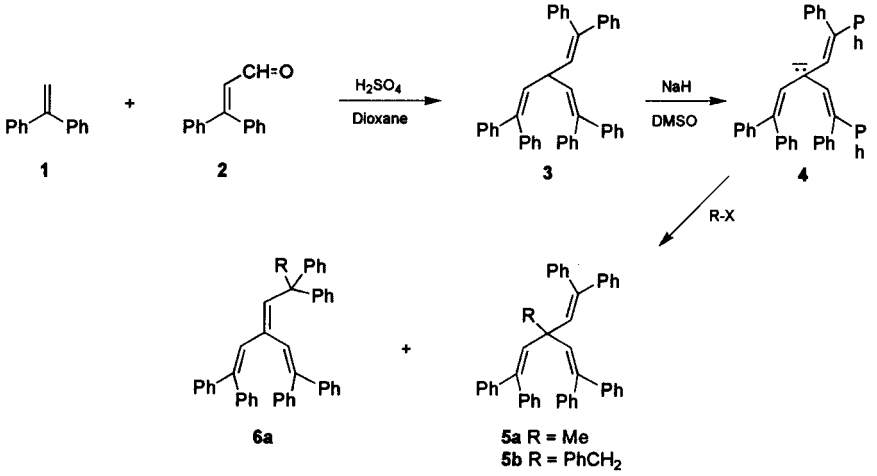
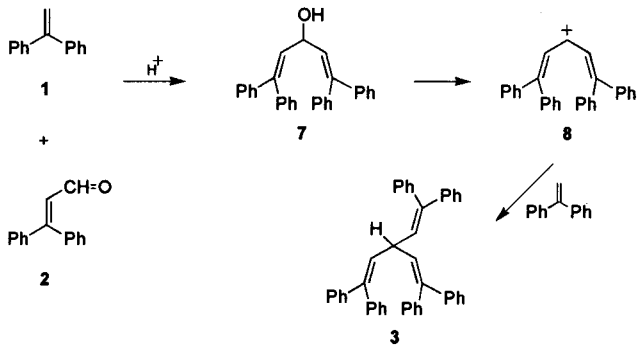
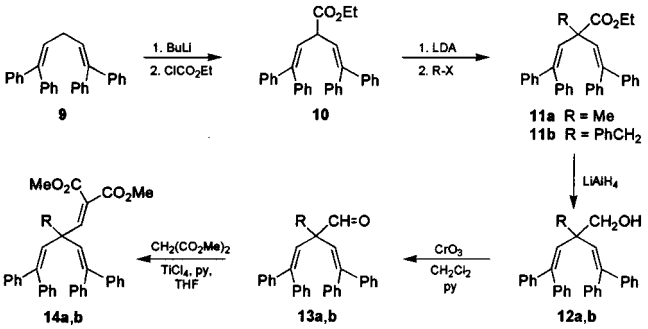
Scheme 1. Synthesis of the Tri-π-methanes (R-X for 5a Me-I, for 5b $PhCH_2Br$)



Scheme 2. Reaction Mechanism of the Tri-π-methane Synthesis



Scheme 3. Synthesis of Diesters 14a and 14b

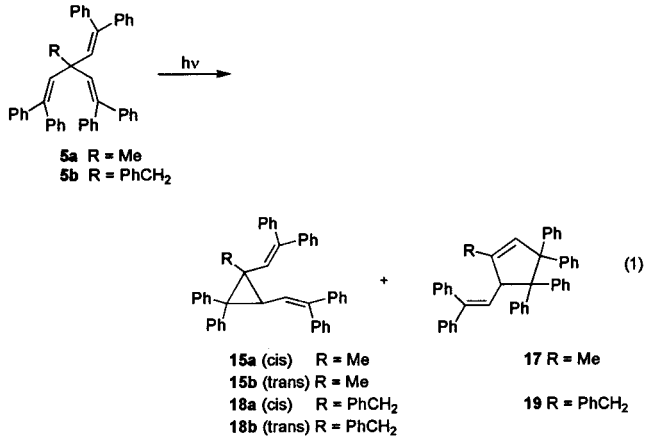


The tris-diphenylvinylmethane **3** reacted with the dimsyl anion in DMSO to afford a deep blue[10] solution of the delocalized carbanion **4**. This reacted smoothly with alkyl and benzyl halides to afford the centrally substituted tri-π-methanes **5a** (R = Me) and **5b** (R = CH_2Ph). Finally, the tri-π-methanes **14a** and **14b** were desired, and the synthesis is outlined in Scheme 3.[11]

Rearrangement Photochemistry. Direct irradiation of tri-π-methane **5a** led smoothly to three photoproducts in a ratio depending on the extent of conversion. Two, **15a** and **15b**, were easily recognized as ordinary, cis and trans, di-π-methane rearrangement products. These were first identified by their characteristic NMR spectra with an AB quartet deriving from a cyclopropyl methine and a diphenylvinyl hydrogen and also an unsplit diphenylvinyl hydrogen. The structure of the cis stereoisomer **15a** was established from permanganate oxidation of the diphenylvinyl side chain to afford the known[6] *cis*-1-methyl-3,3-diphenylcyclopropane-1,2-dicarboxylic acid **16**. The trans stereoisomer **15b** similarly had an NMR spectrum exhibiting two vinyl hydrogens and one methine coupling with the adjacent vinyl hydrogen. Note the Experimental Section. The third photoproduct proved to be more interesting. The NMR spectrum suggested a substituted five-ring structure, and this was confirmed by X-ray as 1-methyl-3,3,4,4-tetraphenyl-5-(2,2-diphenylvinyl)-1-cyclopentene (**17**). This is termed a tri-π-methane product. Its ratio to the di-π-methane photoproducts ranged from 1:1 to 1:2 depending on extent of conversion (vide infra).

In contrast, acetophenone-sensitized irradiation of the tri-π-methane reactant **5a** led primarily (10:1) to the stereoisomeric three-ring di-π-methane products **15**.

Thus, initially it appeared that, at least in the direct irradiation, a tri-π-methane rearrangement had been uncovered. This turns out to be correct. However, as discussed below, there is evidence that some of the tri-π-methane product results from a secondary rearrangement of the less dramatic di-π-methane product (i.e., **15**). The tri-π-methane reaction is shown in eq 1.



In similar fashion, the 3-benzyl tri-π-methane reactant **5b** led to both di-π-methane **18** and tri-π-methane **19**

(10) Kuhn, R.; Rewicki, D. *Justus Liebigs Ann. Chem.* **1965**, *690*, 50−78.

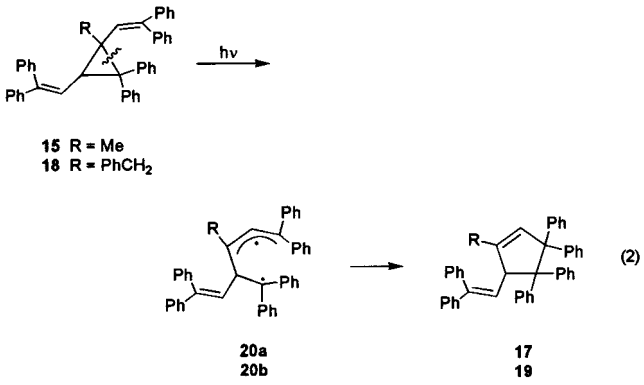
(11) (a) Central protonation as a general phenomenon has a quantum mechanical basis due to maximal electron density.[11b,c] (b) Base Catalyzed Rearrangements. In *Molecular Rearrangements*; Zimmerman, H. E., DeMayo, P., Eds.; Interscience: New York, 1963; Chapter 6, pp 345−406 (see especially pp 345−347). (c) *Quantum Mechanics for Organic Chemists*; Zimmerman, H. E., Ed.; Academic Press: New York, 1975; pp 154−155.

Table 1. Photoproducts Obtained on Direct Irradiation. Distribution at Complete Reaction

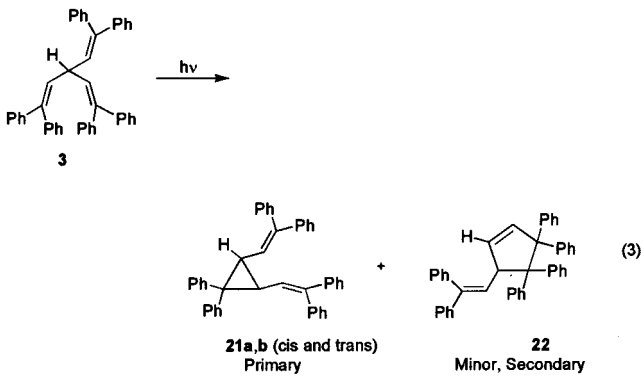
	di-π-methane product		
reactant	cis	trans	tri-π-methane product
methyl tri-π **5a**	49	19	32
benzyl tri-π **5b**	31	17	52

photoproducts on direct irradiation; however, in this case the tri-π-methane product **19** predominated more heavily; note Table 1. It was also observed that the *cis*- and *trans*-di-π-methane stereoisomers were photochemically interconverted approximately 25 times as rapidly as they were formed. Again as in the methyl example, the acetophenone-sensitized reaction of the tri-π-methane reactant **5b** led predominately (75:20) to di-π-methane photoproduct (i.e., **18**).

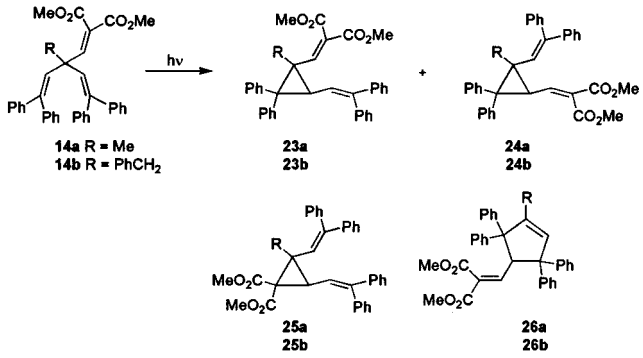
At this point, one would have concluded that in the direct irradiation there were two reactions proceeding in parallel, the ordinary di-π-methane rearrangement and the sought after tri-π-methane rearrangement. However, it was observed that direct photolysis of the di-π-methane photoproducts **15** and **18** led to the tri-π-methane photoproducts **17** and **19** as well as undergoing the rapid cis−trans interconversion (vide supra). Furthermore, the relative amount of tri-π-methane photoproducts increased with the extent of conversion until at very high conversions these predominated (eq 2).



The parent tri-π-methane **3**, lacking a central methyl or benzyl group, exhibited similar photochemistry but with the di-π-methane product **21** being formed at low conversions and with very minor five-ring product **22** being seen only at high conversions. The structure of **21** was established by permanganate oxidation. Equation 3 describes the rearrangement.

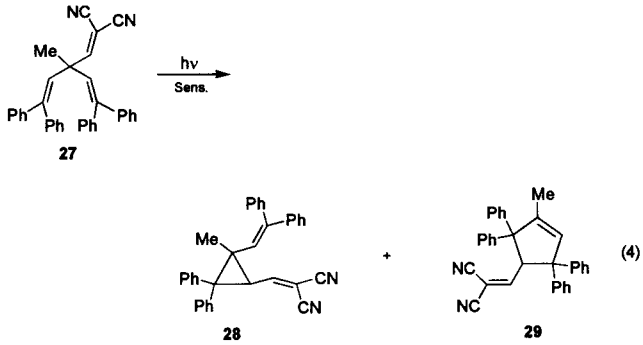


Scheme 4. Photorearrangement of the Dicarbomethoxy Tri-π-methane Reactants 14[a]



[a] Cyclopentene **26** is formed only on sensitization.

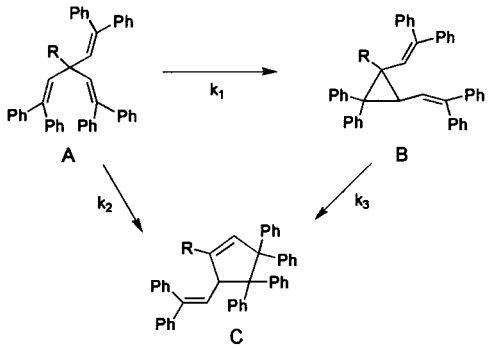
Also studied were the dicarbomethoxy trienes **14a** (R = Me) and **14b** (R = $PhCH_2$) (Scheme 4). Interestingly, on direct irradiation only di-π-methane photoproducts **23**−**25** were formed, while on sensitized irradiation, a cyclopentene photoproduct **26** was also formed. The ratio of the three- to five-ring photoproducts was initially in favor of the di-π-methane photoproduct **24** but at higher conversions favoring the five-ring photoproduct **26**. With further comment to follow in the Discussion, we merely note that this five-membered ring does not have a structure anticipated from a tri-π-methane rearrangement (Scheme 4). Also of interest was the case of the dicyano tri-π-methane **27**, which we studied earlier.[5] In addition to the di-π-methane photoproduct **28** which was previously observed, on extended sensitized photolysis, the five-ring photoproduct **29** was obtained; eq 4. The



mode of formation of this compound along with the dicarbomethoxy product **26** is considered in the Discussion but as in the case of the dicarbomethoxy series, for the present, it is sufficient to note, as in the case of the dicarbomethoxy product **26**, that this product is not a tri-π-methane rearrangement photoproduct.

Kinetic Aspects. The question has been posed above whether the cyclopentene photoproducts arise directly via a tri-π-methane rearrangement or only as a consequence of a secondary reaction of the di-π-methane (i.e., vinylcyclopropane) photoproducts; see Scheme 5. The situation is complicated somewhat by the presence of cis and trans stereoisomers of the cyclopropanes. However, these are rapidly equilibrated and can be treated kinetically as a single species. One example of the product variation with time is given in Scheme 6. The remainder of such kinetic plots are given in the Supporting Information. We note differential light absorption by the reacting species due to three diphenylvinyl groups being present in A and only

Scheme 5. Alternative Reaction Pathways Leading to Tri-π-methane Products



two in B. Thus, it was of interest to make use of naphthalene singlet sensitization with the objective of having a single chromophore absorbing. However, there is the possibility of differential singlet energy transfer efficiencies, again giving rise to differential excitation. Of the two approaches, the direct light absorption seems preferable since only a known factor of 2:3 is involved. Kinetics of the type shown in Scheme 5 seem not to have been solved analytically previously.[12a] Equation 5 gives the analytical solution, and the details are given in Supporting Information.

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

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

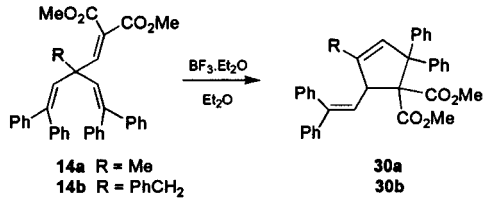
$$\begin{bmatrix} \Delta B_1 \\ \Delta B_2 \\ \Delta B_3 \\ \vdots \end{bmatrix} = \begin{bmatrix} (\partial B_1/\partial k_1) & (\partial B_1/\partial k_2) & (\partial B_1/\partial k_3) \\ (\partial B_2/\partial k_1) & (\partial B_2/\partial k_2) & (\partial B_2/\partial k_3) \\ (\partial B_3/\partial k_1) & (\partial B_3/\partial k_2) & (\partial B_3/\partial k_3) \\ \vdots & \vdots & \vdots \end{bmatrix} \begin{bmatrix} \Delta k_1 \\ \Delta k_2 \\ \Delta k_3 \end{bmatrix} \qquad (6b)$$

$$\Delta\mathbf{B} = \mathbf{F}\Delta\mathbf{k} \qquad (6c)$$

$$\Delta\mathbf{k} = (\mathbf{F}^t\mathbf{F})^{-1}\mathbf{F}^t\Delta\mathbf{B} \qquad (6d)$$

Here the ΔB_t term in eq 6a is just the deviation, at a single time t, of the experimental concentration of B from the theoretical value, as given by eq 5. Equation 6b merely gives this variation at all of the reaction times of interest, and this equation is written more simply as eq 6c. The partial derivatives in eqs 6a and 6b are also derived in the Supporting Information. Corresponding to each deviation ΔB_t of a concentration of B at time t, there is an error in the rate constants k_1, k_2, and k_3. A solution for the column vector $\Delta\mathbf{k}$ gives the corrections in the three rate constants needed to reduce the errors in the B concentrations over the observation period as given in the column vector $\Delta\mathbf{B}$. The solution for the $\Delta\mathbf{k}$ vector is given by eq 6d where $\mathbf{F}$ is the matrix of partial derivatives in eq 6b and $\mathbf{F}^t$ is the tranpose. However, all of these expressions involve k_1, k_2, and k_3, and therefore, it is necessary to employ an initial guess (e.g., 0.5, 0.5, 0.5) for these. Then eq 6d in the computer program affords a better approximation of the k's. For fitting the theoretical expression to the experimental data an iterative computer solution was utilized employing our program ABC_Kinetics.[12c] At convergence, the rate constants prove nicely independent of the choice for initial guess values. The results are given in Table 2.

Ground-State Tri-π-methane Rearrangements. Although this study primarily focused on excited-state chemistry, serendipitously two examples of a ground-state counterpart were encountered in the course of our synthetic efforts. It was found that boron trifluoride etherate catalyzed the rearrangement of the tri-π-methane systems **14a**,**b** to afford five-membered ring products **30a**,**b**. Actually, the rearrangement to **30a** was detected originally in very minor (ca. 3%) yield as a byproduct of the synthesis of tri-π-methane reactant **14a**. Although these products did not arise in excited-state processes, they were independently intriguing. This rearrangement is shown in eq 7, and the reaction mechanisms are considered in the Discussion. However, at this point it is sufficient to state that the nature of the molecular rearrangements in this ground-state chemistry is quite different from that encountered in the photochemical processes.



(7)

Interpretative Discussion

The Tri-π-methane Rearrangement. The first item requiring mention is the observation of the desired but elusive tri-π-methane photoproduct. But as noted in eq 2, there exists a mechanism for conversion of the di-π-methane photoproducts, e.g., **15** and **18**, to afford the tri-π-methane structures **17** and **19**. If this is the only source of tri-π-methane product, then there would be no real tri-π-methane rearrangement.

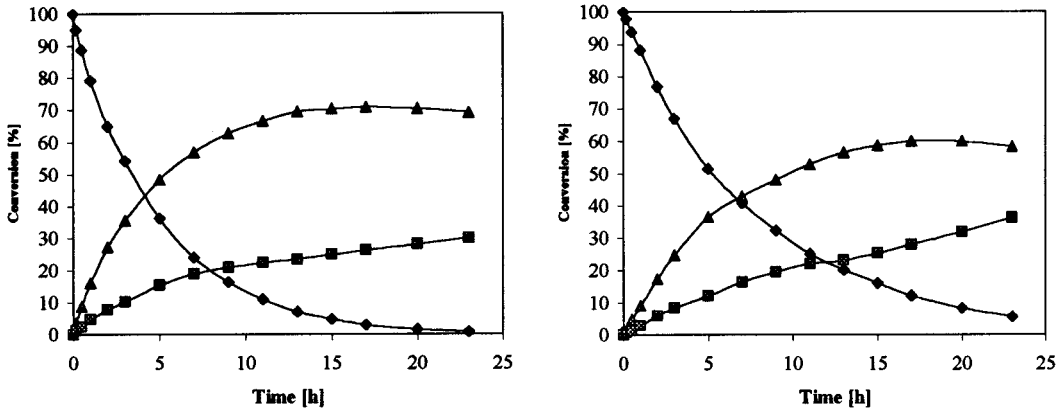
However, the kinetic treatment dissects the indirect and the direct routes to the tri-π-methane product; see Scheme 5 where k_1 leads to the di-π-methane photoproduct (B in Scheme 5), k_2 leads to the tri-π-methane photoproduct C, and k_3 corresponds to the conversion of initially formed di-π-methane to tri-π-methane product. Reference to Table 2 shows that k_2 heavily predominates in all cases over k_3, demonstrating that most of the five-membered-ring product truly comes from a direct tri-π-methane reaction and that the isomerization process (B → C) proceeds rather slowly.[13]

One point of interest is the mechanism of conversion of the di-π-methane to the tri-π-methane products. In this context, we see that there are two diradicals available from three-ring opening. Opening of bond **a** leads to **20**,

(12) (a) The solution of these kinetics was not found in a search of physical chemistry textbooks and the literature. However, elegant general theory for complex kinetics using an eigenvalue method is described in ref 12b. and applied to a less complex case. In our hands, this approach affords the same result as in eq 5 but is cumbersome and requires special linear combinations of the eigenvectors. Thus, the method described here seems worthwhile to have in the literature. (b) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*; Wiley: New York, 1981. (c) Zimmerman, H. E. Unpublished results. The Supporting Information gives a flow diagram.

(13) We recognize that the rate constants k_1, k_2, and k_3 may be treated as relative rates but actually represent the product of quantum yield and the amount of excitation delivered to each compound.

Scheme 6. Variation of A−C with Time[a]

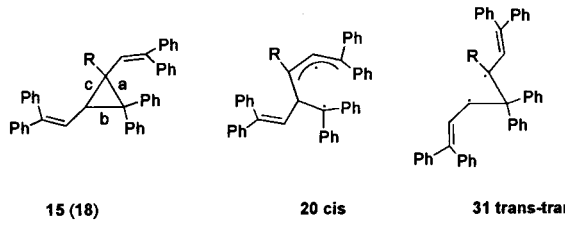


[a] Diamonds are for the tri-π-methane reactant, triangles are for di-π-methane, and squares are for tri-π-methane photoproducts: left, R = methyl; right, R = benzyl. Both with naphthalene sensitizer.

Table 2. Representative Relative Rate Constants

		observed relative rate constants		
tri-π-methane reactant	sensitizer	k_1	k_2	k_3
4-methyl tri-π-methane	none	0.102	0.045	0.001
	naphthalene	0.163	0.053	0.004
4-benzyl tri-π-methane	none	0.223	0.143	0.024
	naphthalene	0.099	0.028	0.014
4-hydrogen tri-π-methane	none	0.018	0.003	0.001
	naphthalene	0.102	0.001	0.001

Scheme 7. Two Alternative Diradicals Available from Three-Ring Opening

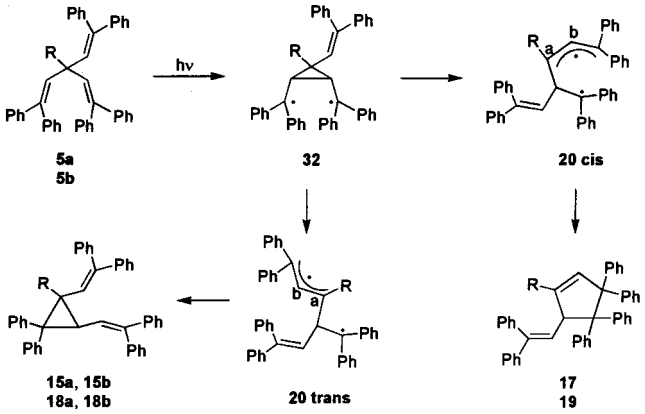


the less delocalized of two diradicals. Alternatively, scission of bond **c** affords the more delocalized diradical **31**. This diradical (see Scheme 7) is the intermediate in the rapid cis−trans interconversion but is irrelevant to the tri-π-methane rearrangement.

The preferred stereochemistry of three-ring opening leads to the trans−trans diallylic diradical **31**, which cannot close to a five-membered ring. Of the remaining bonds **a** and **b**, breakage of **a** does lead to the next most stable diradical with diphenylvinyl and benzhydryl delocalization as well as having an alkyl group R at a diradical center. Thus, conversion of the three-membered ring isomer **15** (or **18**) to the tri-π-methane five-ring product **17** (or **19**) product is understood as arising from fission of bond **a** followed by bond formation between the two benzhydryl centers of diradical **20**.

In the mechanism for the tri-π-methane rearrangement we see (see Scheme 8) that there is a conformational effect. The opening of cyclopropyldicarbinyl diradical **32** can lead to either of two allylic conformations (Scheme 8), with only the cisoid conformer **20 cis** (see Scheme 8, cisoid bond a−b) being able to close to afford the five-membered ring. The transoid diradical **20 trans** (Scheme 8, bond a−b) on such closure would have a trans double bond in the five-membered ring. Both isomers (**20 cis** and

Scheme 8. Mechanism of the Tri-π-methane Rearrangement in Competition with the Di-π-methane Process



20 trans) are capable of closing 1,3 to afford the di-π-methane products (**15** and **18**).[14]

Interestingly, the triplet of the tri-π-methane reactants generated by sensitization exhibit primarily the di-π-methane rearrangement. This seems likely to result from selective opening with transoid allylic stereochemistry. One might anticipate that the transoid diradical would be preferred by the triplet as a consequence of the greater odd-electron separation compared with cisoid geometry. This is an example of exchange integral singlet−triplet control.[15] See Figure 1. Thus, it has been noted that, where there is multiplicity dependence of photochemical reaction course, one can consider two types of reactions—"small K" reactions and "large K" reactions where "K" is the quantum mechanical exchange integral controlling the S_1-T_1 energy gap on the reaction hypersurface. A number of different reaction types have been empirically categorized as "small K" or "large K" varieties.[15] Reactions involving diradical species lacking polar groups are of the "large K" type. The generalization has been stated that triplets prefer large K reactions and singlets prefer

(14) The stereochemistry of cyclopropyldicarbinyl diradical **32** is not presently defined, but as a consequence of free rotation about single bonds, this is not relevant here.

(15) (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.

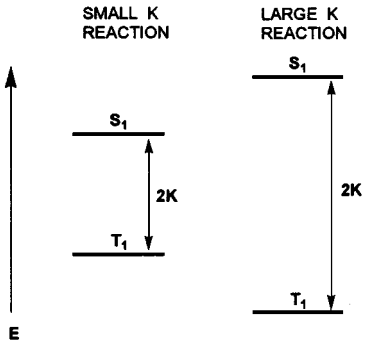


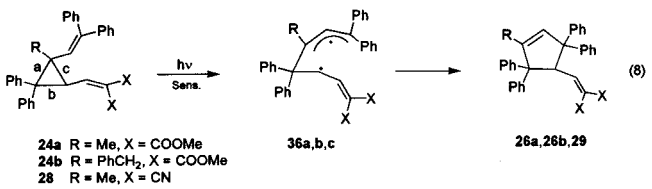
Figure 1. Exchange integral control of reactions by multiplicity.

small K reactions. Figure 1 makes clear that this is just a matter of the reacting species selecting the lower energy of two pathways. Of course, other factors, such as steric effects, may override the generalization in cases.

Also, an interesting observation is that the tri-π-methane systems proved perfectly reactive despite the presence of potential "free-rotors"[16] (i.e., the diphenylvinyl groups). The normal rapid triplet decay due to free-rotor effects generally seems to diminish with increased steric congestion as in the present systems where the diphenylvinyl groups have inhibited rotation.

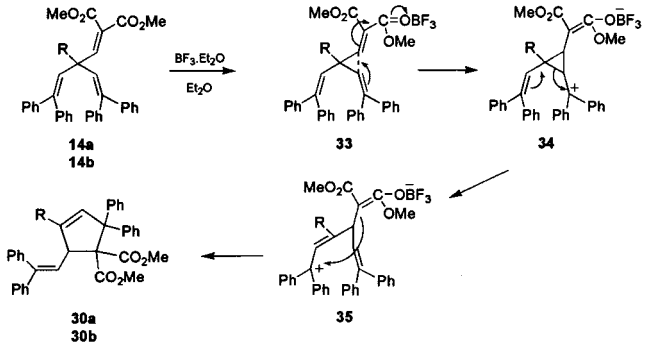
One further observation is that the ratio k_2/k_3 (see Scheme 5) diminishes as the group R becomes larger, thus forcing the benzhydryl odd-electron center trans. The initial thought is that as R become larger, ring opening of the cyclopropyldicarbinyl diradical would afford more of the cisoid allylic moiety, thus favoring k_2 and the tri-π-methane route. This clearly is the case where the "methane carbon" bears only a hydrogen as in reactant **3** (see eq 3) and where almost exclusively di-π-methane rearrangement occurs. Referring to Scheme 8, we can see that if R is hydrogen, opening of the cyclopropyldicarbinyl diradical **32** should prefer the route leading to the transoid allylic diradical **20 trans** for steric reasons. Also, closure to the three-ring product **15** and **18** does not place four large groups on adjacent carbons.

A final observation is that for the dicarbomethoxy and dicyano di-π-methane conversions to five-ring products (i.e., **26** and **29**; eq 8), the five-ring products are not those which arise from a tri-π-methane rearrangement. The diradical intermediates **36a**−**c** are counterparts of the diradical **31** (see Scheme 7) utilized in the cis−trans isomerization discussed for the all hydrocarbon cases. However, in this instance, the diradical closes to form the observed five-membered ring products **26a**, **26b**, and **29**, a closure not encountered in absense of the electron-withdrawing carbomethoxy and cyano groups. One rationale is that in the hydrocarbon examples it is the transoid diradical which is formed as a result of lesser steric interactions while the carbomethoxy and cyano diradicals are cisoid due to the polar groups and charge separation being minimized in the cisoid conformation.



(8)

Scheme 9. Mechanism of the BF_3-Catalyzed Tri-π-methane Rearrangement



Ground-State Tri-π-methane Rearrangement. Interestingly, the ground-state counterpart tri-π-methane rearrangement proceeded by a different mechanism: that outlined in Scheme 9. The boron trifluoride coordination with the carbomethoxy carbonyl oxygen is unexceptional. The bonding to form the cyclopropylcarbinyl cationic zwitterion **34** as an intermediate merely provides a mechanism for the 1,2-diphenylvinyl shift leading to the five-membered ring products **30**; aryl and vinyl 1,2-migrations normally proceed via such bridged species. This mechanism, however, is a different one than that involved in the tri-π-methane rearrangement.

Conclusion

The di-π-methane rearrangement has become one of the useful and widely employed organic reactions to generate three-membered rings. Now there is a counterpart tri-π-methane reaction leading to five-membered ring compounds. The present study has dealt with the problems of multiplicity control, the presence of two pathways to the tri-π-methane products, a ground-state tri-π-methane analogue, and the solution to an interesting kinetic problem.

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. Preparative thick-layer chromatography was carried out with silica gel coated on glass (Sigma, type H, 10−40 μm, mixed with fluorescent indicator (1%) and gypsum binder (10%), 50 g of silica gel, and 105 mL of water per plate, 20 × 20 cm). Plates were dried 24 h after preparation at room temperature. Neutral workup refers to dilution with the indicated solvent, successive washing with distilled water and brine, drying over anhydrous magnesium sulfate, and filtering. Basic workup added an initial saturated $NaHCO_3$ wash after dilution with water. Acidic workup added an initial 5% HCl wash after dilution with water. 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

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prior to use. ^{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 elemental analyses were performed by the Chemisar Laboratories, Inc. (Guelph, ON, Canada). The high-resolution electron impact mass spectra (MS) were run at 150 °C source temperature on a MS50TC ultrahigh-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 at the University of Wisconsin, Biochemistry Department.

General Procedure for Kinetic Photolyses. Kinetic solution photolyses were carried out in sealed NMR tubes (17 cm of length and 0.5 cm o.d.) in benzene-d_6 under nitrogen. The tube was irradiated in the black-box apparatus.[17] 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) allowing a 300−350 nm band-pass. 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. 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.

General Procedure for Solid-State Photolyses. Solid-state photolyses were carried out with a thin layer of crystals between two quartz plates. The plates were placed to the cooling wall of the photochemical reactor, and the edges were tied up with Parafilm tape. The cooling wall was placed into the reactor flask filled with water-ice mixture. The temperature of the filter solution and water in the photoreactor was kept between 15 and 20 °C. Most of the irradiated crystals was recovered mechanically, and the rest was obtained by quick washing of the plates with a small amount of appropriate solvent.

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 corrections were applied, and each structure was solved with the appropriate space group symmetry by direct methods using SHELXTL[18a] and SHELXS.[18b] 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 coordinates and the Crystallographic Information Files (cif-files) for all compounds studied by X-ray crystallography were deposited with the Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge, CB2 1EZ, U.K.

3-(2,2-Diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (3). To a solution of 7.22 g (40 mmol) of 1,1-diphenylethylene and 4.16 g (20 mmol) of 3,3-diphenyl-2-propenal[19−20] in 50 mL of anhyd dioxane was added 0.50 mL of concd sulfuric acid. The solution turned deep blue and then brown and was heated to reflux for 6 h and then stirred for 12 h at room temperature. The dioxane was removed in vacuo to afford a violet oil which was filtered through a 5 × 10 cm plug of Florisil and then through a 5 × 10 cm plug of Alumina with dichloromethane as eluent. Concentration in vacuo afforded a yellow oil which was crystallized from dichloromethane/methanol (1:2) to yield 9.41 g (85%) of 3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**3**) as colorless plates, mp 226−228 °C (lit.[7b] mp 228−230 °C (*n*-BuOH)).

The spectral characteristics were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40−7.05 (m, 18H, arom), 6.91 (t, 6H, J = 8 Hz, arom), 6.70 (dd, 6H, J = 7.5, 1.5 Hz, arom), 6.05 (d, 3H, J = 10 Hz, 3 × CH═), 4.33 (q, 1H, J = 10 Hz, CH); ^{1}H NMR (benzene-d_6, 300 MHz) δ 7.31−6.78 (m, 30H, arom), 6.07 (d, 3H, J = 10 Hz, CH═), 4.61 (q, 1H, J = 10 Hz, CH); UV (hexane) λ(max) = 268 nm (ϵ = 34 560), λ(shoulder) = 236 nm (ϵ = 33 160), λ = 300 nm (ϵ = 7062); MS *m/e* 550.2674 (calcd for $C_{43}H_{34}$, 550.2661). The structure assignment was confirmed by X-ray crystallography (see the Supporting Information).

3-Methyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (5a). To a mixture of 0.48 g (20 mmol) of sodium hydride in 100 mL of anhyd DMSO at 0 °C was added 5.51 g (10 mmol) of 3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**3**) in 50 mL of anhyd DMSO. After the deep blue solution was stirred for 6 h at room temperature, 5.68 g (40 mol, 2.49 mL) of methyl iodide was added quickly. The DMSO solution was diluted with water and then ether extracted. Concentration of the extracts in vacuo afforded a brown oil which was filtered through a 5 × 10 cm plug of Florisil and then through a 5 × 10 cm plug of alumina with dichloromethane as eluent. Concentration in vacuo afforded a yellow oil which was crystallized from cold methanol/ethyl acetate/ether (2:1:1) to give 2.26 g (40%) of 3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,3-hexadiene (**6a**) as colorless plates, mp 80−82 °C (at 60 °C solvated diethyl ether was lost). The filtrate, on concentration and crystallization from methanol/dichloromethane (2:1), yielded 2.49 g (44%) of 3-methyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**5a**) as colorless prisms, mp 115−117 °C.

The spectral characteristics of 3-methyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**5a**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.30−7.08 (m, 24H, arom), 6.83−6.73 (m, 6H, arom), 5.97 (s, 3H, CH═), 1.13 (s, 3H, CH_3); ^{1}H NMR (benzene-d_6, 300 MHz) δ 7.26−7.20 (m, 6H, arom), 7.12−6.92 (m, 24H, arom), 6.17 (s, 3H, CH═), 1.28 (s, 3H, CH_3); UV (hexane) λ(max) = 260 nm (ϵ = 31 430), λ = 300 nm (ϵ = 3530); MS *m/e* 564.2805 (calcd for $C_{44}H_{36}$, 564.2817). Anal. Calcd for $C_{44}H_{36}$: C, 93.57; H, 6.43. Found: C, 93.52; H, 6.47. The structure assignment was confirmed by X-ray crystallography (see the Supporting Information).

The spectral characteristics of 3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,3-hexadiene (**6a**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31−6.96 (m, 26H, arom), 6.63−6.55 (m, 2H, arom), 6.42 (t, 1H, J = 1.47 Hz, ═CHCMe), 6.40−6.33 (m, 2H, arom), 6.13 (d, 1H, J = 1.47 Hz, CH═), 5.79 (d, 1H, J = 1.47 Hz, CH═), 1.89 (s, 3H, CH_3); ^{1}H NMR (benzene-d_6, 300 MHz) δ 7.25−6.87 (m, 26H, arom), 6.85−6.75 (m, 2H, arom), 6.67−6.57 (m, 2H, arom), 6.47 (t, 1H, J = 1.5 Hz, CH═CMe), 6.26 (d, 1H, J = 1.5 Hz, CH═), 6.05 (d, 1H, J = 1.5 Hz, CH), 1.85 (s, 3H, CH_3); UV (hexane) λ(max) = 302 nm (ϵ = 25 629), λ(shoulder) = 236 nm (ϵ = 26 750), λ = 325 nm (ϵ = 14 120); MS *m/e* 564.2852 (calcd for $C_{44}H_{36}$, 564.2817). The structure assignment was confirmed by X-ray crystallography (see the Supporting Information).

3-Benzyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (5b). To a suspension of 0.24 g (10 mmol) of sodium hydride in 50 mL of anhyd DMSO was added 2.75 g (5.0 mmol) of 3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**3**) in 25 mL of anhyd DMSO. After the deep blue solution was stirred for 12 h at room temperature, 3.42 g (20 mmol, 2.38 mL) of benzyl bromide was added quickly. The DMSO was diluted with water and ether extracted. Concentration of the extracts in vacuo afforded a brown oil which was filtered through a 5 × 10 cm plug of silica gel with dichloromethane as eluent. Concentration in vacuo and crystallization from methanol/dichloromethane (2:1) yielded 2.55 g (80%) of 3-benzyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**5b**) as colorless prisms, mp 182−183 °C (at 90−95 °C solvated methanol was lost).

The spectral characteristics were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.26−6.98 (m, 29H, arom), 6.70−6.62 (m, 6H, arom) 5.92 (s, 3H, CH═), 3.00 (s, 2H, CH_2Ph); ^{1}H NMR (benzene-d_6, 300 MHz) δ 7.30−7.24 (m, 2H, arom), 7.19−6.94 (m, 27H, arom), 6.91−6.82 (m, 6H, arom) 6.19 (s, 3H, CH═),

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4.26 (s, 3H, CH_3OH), 3.17 (s, 2H, CH_2Ph); UV (hexane) λ(max) = 263 nm (ϵ = 32 720), λ = 300 nm (ϵ = 3740); MS *m/e* 640.3139 (calcd for $C_{50}H_{40}$, 640.3130). Anal. Calcd for $C_{51}H_{44}O$: C, 91.03; H, 6.59. Found: C, 91.41; H, 6.24.

Ethyl 2-(2,2-Diphenylvinyl)-4,4-diphenyl-3-butenoate (10).[6b] A solution of 18.63 g (50 mmol) of 1,1,5,5-tetraphenyl-1,4-pentadiene (**9**)[21,22] in 100 mL of anhyd THF was cooled to 0 °C, and 30 mL (60 mmol) of 2.0 M *n*-butyllithium in pentane was added dropwise. After the deep blue solution was stirred for 30 min at 0 °C, 7.05 g (65 mmol, 6.22 mL) of ethyl chloroformate was added. The reaction was allowed to stir and warm to ambient temperature, during which time the color changed to red violet. Basic workup and concentration in vacuo afforded a brown-yellow solid. Recrystallization from ethanol yielded 18.45 g (83%) of ethyl 2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenoate (**10**) as colorless crystals, mp 94−95 °C.

The spectral characteristics were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35−7.05 (m, 16H, arom), 7.00−6.91 (m, 4H, arom), 6.19 (d, 2H, J = 10.2 Hz, CH═), 4.19 (t, 1H, J = 10.2 Hz, CH), 4.15 (q, 2H, J = 7.3 Hz, CH_2OCO), 1.27 (t, 3H, J = 7.3 Hz, CH_3); MS *m/e* 444.2102 (calcd for $C_{32}H_{28}O_2$, 444.2089).

Ethyl 2-Methyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenoate (11a).[6b] To a solution of 8.10 g (80 mmol, 11.21 mL) of diisopropylamine in 300 mL of anhyd THF at −10 °C (ice−MeOH) was added dropwise 24 mL (48 mmol) of 2.0 M *n*-butyllithium in pentane. After the mixture was stirred for 20 min, a solution of 17.78 g (40 mmol) of ethyl 2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenoate (**10**) in 100 mL of anhyd THF was added dropwise via cannula. The solution turned brown and was allowed to warm to 10 °C, when 22.71 g (160 mmol, 9.96 mL) of methyl iodide was added. The resulting solution was stirred 1 h at room temperature before being quenched with addition of 10% hydrochloric acid. Basic workup and concentration in vacuo afforded a brown-yellow solid. Recrystallization from ethanol yielded 15.62 g (85%) of ethyl 2-methyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenoate (**11a**) as colorless needles, mp 89−90 °C.

The spectral characteristics were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.28−7.13 (m, 16H, arom), 7.08−7.02 (m, 4H, arom), 6.22 (s, 2H, CH═), 3.67 (q, 2H, J = 7.3 Hz, CH_2-OCO), 1.40 (s, 3H, CH_3), 1.11 (t, 3H, J = 7.3 Hz, CH_3); MS *m/e* 458.2254 (calcd for $C_{33}H_{30}O_2$, 458.2246.

2-Methyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenol (12a).[6b] To a suspension of 6.08 g (160 mmol) of lithium aluminum hydride in 200 mL of anhyd THF at 0 °C was added 18.34 g (40 mmol) of ethyl 2-methyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenoate (**11a**) in 100 mL of anhyd THF. The reaction mixture immediately turned blue-green and was allowed to stir for 2 h. The excess of lithium aluminum hydride was quenched by cautious addition of 3.0 mL of water and then 4.0 mL of 1.0 M NaOH via syringe. The gray solid was filtered and washed with 200 mL of ether. The filtrate was dried and concentrated in vacuo afforded a clear oil which was crystallized from ethanol (ca. 50 mL), yielding 14.0 g (84%) of 2-methyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenol (**12a**) as colorless crystals, mp 120−122 °C.

The spectral characteristics were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31−7.11 (m, 16H, arom), 7.07−6.97 (m, 4H, arom), 5.88 (s, 2H, CH═), 3.37 (s, 2H, CH_2O), 1.52 (bs, 1H, OH), 0.99 (s, 3H, CH_3); MS *m/e* 416.2130 (calcd for $C_{31}H_{28}O$, 416.2140.

2-Methyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenal (13a).[6b] To a solution of 47.5 g (0.60 mol, 48.6 mL) of pyridine in 300 mL of dichloromethane at 0 °C was added 30.0 g (0.30 mol) of chromium trioxide. After the mixture was stirred for 45 min, a solution of 12.51 g (0.03 mol) of 2-methyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenol (**12a**) in 60 mL of dichloromethane was added dropwise and allowed to stir for 2.5 h. The liquid was decanted and the black residue was thoroughly washed with 200 mL of dichloromethane. The organic phases were washed with 1.0 M NaOH (3 × 150 mL), 5% HCl (3 × 150 mL), water (3 × 150 mL) and 150 mL of saturated $NaHCO_3$. The extracts were dried and filtered through a 4 × 10 cm plug of Florisil. Concentration in vacuo and crystallization from hexane (ca. 200 mL) yielded 10.45 g (84%) of 2-methyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenal (**13a**) as colorless plates, mp 108−109 °C.

The spectral characteristics[23] were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.02 (s, 1H, CH═O), 7.35−7.03 (m, 20H, arom), 6.06 (s, 2H, CH═), 1.30 (s, 3H, CH_3); UV (hexane) λ-(max) = 258 nm (ϵ = 26 615), λ = 300 nm (ϵ = 2083); MS *m/e* 414.1975 (calcd for $C_{31}H_{26}O$, 414.1984).

Methyl 2-Carbomethoxy-4-methyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate (14a). To a solution of 50 mL of anhyd THF at 0 °C was added 2.85 g (15 mmol, 1.65 mL) of titanium tetrachloride[15b,24] in 4.0 mL of tetrachloromethane. To this yellow mixture was added 0.87 g (6.6 mmol, 0.75 mL) of dimethyl malonate and 2.49 g (6.0 mmol) of 2-methyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenal (**13a**) in 10 mL of anhyd THF. The mixture was allowed to stir at 0 °C for 20 min followed by addition of 2.37 g (30 mmol, 2.42 mL) of anhyd pyridine. The brown solution was allowed to warm to room temperature, stirred an additional 13 h, diluted with 30 mL of water, and poured into 100 mL of ether. The aqueous layer was ether extracted, and the combined organic phases were washed with water, sodium bicarbonate, and brine, dried, and concentrated in vacuo leaving 3.20 g of yellow oil. Chromatography of the crude product on a 3 × 120 cm silica gel column eluted with 20% ethyl acetate in hexane gave 2.61 g (82%, R_f = 0.61) of methyl 2-carbomethoxy-4-methyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate (**14a**) as a viscous oil and 95 mg (3%, R_f = 0.69) of 1-methyl-3,3-diphenyl-4,4-dicarbomethoxy-5-(2,2-diphenylvinyl)-1-cyclopentene (**30a**) as white crystals, mp 175−177 °C.

The spectral characteristics of methyl 2-carbomethoxy-4-methyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate (**14a**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40−7.12 (m, 16H, arom), 7.08−6.96 (m, 4H, arom), 6.83 (s, 1H, CH═CCO), 6.00 (s, 2H, CH═CPh), 3.62 (s, 3H, CH_3OCO), 3.50 (s, 3H, CH_3OCO), 1.25 (s, 3H, CH_3); ^{1}H NMR (benzene-d_6, 300 MHz) δ 7.28−7.22 (m, 4H, arom), 7.18−6.99 (m, 16H, arom), 7.03 (s, 1H, CH═CCO), 6.19 (s, 2H, CH═CPh), 3.29 (s, 3H, CH_3OCO), 3.25 (s, 3H, CH_3OCO), 1.30 (s, 3H, CH_3); UV (hexane) λ(max) = 256 nm (ϵ = 22 150); MS *m/e* 528.2303 (calcd for $C_{36}H_{32}O_4$, 528.2301).

The spectral characteristics of 1-methyl-3,3-diphenyl-4,4-dicarbomethoxy-5-(2,2-diphenylvinyl)-1-cyclopentene (**30a**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.80−7.65 (d, 2H, J = 8 Hz, arom), 7.50−7.00 (m, 16H, arom), 6.87−6.75 (m, 2H, arom), 5.97 (bs, 1H, CH═CMe), 5.88 (d, 1H, J = 11 Hz, CH═CPh), 4.81 (d, 1H, J = 11 Hz, CH), 3.32 and 3.15 (2 × s, 6H, CH_3OCO), 1.91 (s, 3H, CH_3); MS *m/e* 528.2315 (calcd for $C_{36}H_{32}O_4$, 528.2301). Anal. Calcd for $C_{36}H_{32}O_4$: C, 81.79; H, 6.10. Found: C, 82.16; H, 6.12. The structure assignment was confirmed by X-ray crystallography (see the Supporting Information).

Ethyl 2-Benzyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenoate (11b). To a solution of 12.14 g (120 mmol, 16.82 mL) of diisopropylamine in 400 mL of anhyd THF at −10 °C (ice−MeOH) was added dropwise 42 mL (84 mmol) of 2.0 M *n*-butyllithium in pentane. After the mixture was stirred for 20 min, a solution of 26.68 g (60 mmol) of ethyl 2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenoate (**10**) in 150 mL of anhyd THF was added dropwise via cannula. The solution turned brown and was allowed to warm to 10 °C, when 12.0 g (70 mmol, 8.34 mL) of benzyl bromide was added. The resulting solution was stirred for 1 h at room temperature before being quenched with addition of 10% hydrochloric acid. Basic workup and concentration in vacuo afforded a brown-yellow oil. Crystallization from ethanol yielded 26.74 g (83%) of ethyl

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(24) Lehnert, W. *Tetrahedron* **1973**, *29*, 635−638.

2-benzyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenoate (**11b**) as colorless needles, mp 117−119 °C.

The spectral characteristics were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.27−7.03 (m, 25H, arom), 6.18 (s, 2H, CH═), 3.42 (q, 2H, J = 7.1 Hz, CH_2OCO), 3.23 (s, 2H, CH_2-Ph), 0.96 (t, 3H, J = 7.1 Hz, CH_3); MS *m/e* 534.2557 (calcd for $C_{39}H_{34}O_2$, 534.2559). Anal. Calcd for $C_{39}H_{34}O_2$: C, 87.61; H, 6.41. Found: C, 87.96; H, 6.34.

2-Benzyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenol (12b). To a suspension of 5.32 g (140 mmol) of lithium aluminum hydride in 200 mL of anhyd THF at 0 °C was added 17.8 g (33.2 mmol) of ethyl 2-benzyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenoate (**11b**) in 100 mL of anhyd THF. The reaction mixture immediately turned blue-green and was stirred for 2 h. 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 via syringe. The gray solid was filtered and washed with 200 mL of ether. The filtrate was dried, and concentration in vacuo afforded a clear oil which was crystallized from ethanol (50 mL), yielding 14.61 g (89%) of 2-benzyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenol (**12b**) as a colorless solid, mp 137−139 °C.

The spectral characteristics were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.28−7.13 (m, 17H, arom), 7.05−6.96 (m, 8H, arom), 5.79 (s, 2H, CH═), 3.12 (d, 2H, J = 6 Hz, CH_2O), 2.98 (s, 2H, CH_2Ph), 1.31 (t, 1H, J = 6 Hz, OH); MS *m/e* 492.2475 (calcd for $C_{37}H_{32}O$, 492.2453). Anal. Calcd for $C_{37}H_{32}O$: C, 90.21; H, 6.55. Found: C, 90.02; H, 6.59.

2-Benzyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenal (13b). To a solution of 44.3 g (0.560 mol, 43.3 mL) of pyridine in 300 mL of dichloromethane at 0 °C was added 28.0 g (0.280 mol) of chromium trioxide. After the mixture was stirred for 45 min, a solution of 13.8 g (0.028 mol) of 2-benzyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenol (**12b**) in 100 mL of dichloromethane was added dropwise and stirred for 2.5 h. The liquid was then decanted and the black residue was thoroughly washed with 200 mL of dichloromethane. The organic phases were then washed with 1.0 M NaOH (3 × 150 mL), 5% HCl (3 × 150 mL), water (3 × 150 mL), and 150 mL of saturated $NaHCO_3$. The extracts were dried and filtered through a 4 × 10 cm plug of Florisil. Concentration in vacuo and crystallization from hexane (ca. 150 mL) yielded 11.6 g (84%) of 2-benzyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenal (**13b**) as colorless plates, mp 139−141 °C.

The spectral characteristics were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.98 (s, 1H, CH═O), 7.37−6.90 (m, 25H, arom), 6.03 (s, 2H, CH═), 3.15 (s, 2H, CH_2Ph); MS *m/e* 490.2286 (calcd for $C_{37}H_{30}O$, 490.2297). Anal. Calcd for $C_{37}H_{30}O$: C, 90.58; H, 6.16. Found: C, 90.96; H, 6.17. The structure assignment was confirmed by X-ray crystallography (see the Supporting Information).

Methyl 2-Carbomethoxy-4-benzyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate (14b). To a solution of 80 mL of anhyd THF at 0 °C was added 2.85 g (15 mmol, 1.65 mL) of titanium tetrachloride[15b,24] in 4.0 mL of tetrachloromethane. To this yellow mixture was added 0.87 g (6.6 mmol, 0.75 mL) of dimethyl malonate and 2.94 g (6 mmol) of 2-benzyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenal (**13b**) in 20 mL of anhyd THF. The mixture was allowed to stir at 0 °C for 20 min followed by addition of 2.37 g (30 mmol, 2.42 mL) of anhyd pyridine. The brown solution was allowed to warm to room temperature, stirred an additional 40 h, diluted with 30 mL of water and poured into 150 mL of ether. The aqueous layer was ether extracted and the combined organic phases were washed with water, sodium bicarbonate, brine, dried and concentrated in vacuo leaving 3.7 g of yellow oil. Chromatography of the crude product on a 5 × 60 cm silica gel column eluted with 10% diethyl ether in hexane gave 0.29 g (10%, R_f = 0.45) of starting aldehyde **13b** and 2.92 g (R_f = 0.58) of crude product as an oil which was crystallized from methanol/acetone (3:1) to afford 2.72 g (83% at 90% conversion) of methyl 2-carbomethoxy-4-benzyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate (**14b**) as colorless crystals, mp 102−103 °C.

The spectral characteristics were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.51−6.91 (m, 25H, arom), 6.68 (s, 1H, CH═CCO), 5.94 (s, 2H, CH═CPh), 3.58 (s, 3H, CH_3OCO), 3.38 (s, 3H, CH_3OCO), 3.08 (s, 2H, CH_2Ph); ^{1}H NMR (benzene-d_6, 300 MHz) δ 7.28−7.22 (m, 2H, arom), 7.18−6.95 (m, 23H, arom), 6.98 (s, 1H, CH═CCO), 6.17 (s, 2H, CH═CPh), 3.23 (s, 3H, CH_3OCO), 3.22 (s, 3H, CH_3OCO), 3.19 (s, 2H, CH_2Ph); UV (hexane) λ(max) = 254 nm (ϵ = 25 400); MS *m/e* 604.2609 (calcd for $C_{42}H_{36}O_4$, 604.2614). Anal. Calcd for $C_{42}H_{36}O_4$: C, 83.42; H, 6.00. Found: C, 83.49; H, 5.90.

Direct Solution Photolysis of 3-Methyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (5a). A solution of 150 mg (0.266 mmol) of 3-methyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**5a**) in 200 mL of benzene was irradiated for 15 min. Concentration in vacuo yielded 160 mg of yellow oil. ^{1}H NMR spectroscopic analysis showed 93% conversion and the composition of the reaction mixture was 52% of cis-cyclopropane **15a**, 11% of trans-cyclopropane **15b** and 30% of cyclopentene **17**. The mixture was crystallized from ethyl acetate/diethyl ether and yielded 82 mg of a mixture of cis−trans isomers **15**. Fractional crystallization from methanol/diethyl ether afforded 55 mg (71%) of *cis*-1-methyl-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**15a**) as colorless thin needles, mp 180−181 °C, and 10 mg (61%) of *trans*-1-methyl-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**15b**) as colorless prisms, mp 165−166 °C.

The spectral characteristics of *cis*-1-methyl-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**15a**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60−6.90 (m, 30H, arom), 6.30 (s, 1H, CH═), 5.80 (d, 1H, J = 10.7 Hz, CH═), 2.35 (d, 1H, J = 10.7 Hz, CH), 0.66 (s, 3H, CH_3); UV (hexane) λ(max) = 262 nm (ϵ = 14 167), λ(shoulder) = 228 nm (ϵ = 17 510), λ = 300 nm (ϵ = 5650); MS *m/e* 564.2810 (calcd for $C_{44}H_{36}$, 564.2817). Anal. Calcd for $C_{44}H_{36}$: C, 93.57; H, 6.43. Found: C, 94.00; H, 6.75.

The spectral characteristics of *trans*-1-methyl-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**15b**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.50−6.80 (m, 30H, arom), 5.81 (s, 1H, CH═), 5.51 (d, 1H, J = 9.9 Hz, CH═), 2.51 (d, 1H, J = 9.9 Hz, CH), 1.42 (s, 3H, CH_3); UV (hexane) λ(max) = 265 nm (ϵ = 14850), λ(shoulder) = 229 nm (ϵ = 23 120), λ = 300 nm (ϵ = 5870); MS *m/e* 564.2808 (calcd for $C_{44}H_{36}$, 564.2817).

Direct Solution Photolysis of 3-Methyl-3-(2,2-diphenyl)vinyl-1,1,5,5-tetraphenyl-1,4-pentadiene (5a). A solution of 150 mg (0.266 mmol) of 3-methyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**5a**) in 200 mL of benzene was irradiated for 1.5 h. Concentration in vacuo yielded 185 mg of yellow oil. ^{1}H NMR spectroscopic analysis showed 100% conversion and the composition of the reaction mixture was 21% of *cis*-cyclopropane **15a**, 4% of *trans*-cyclopropane **15b** and 75% of cyclopentene **17**. The mixture was crystallized from ethyl acetate/diethyl ether and yielded 32 mg of a mixture of cis−trans isomers **15**. The rest was fractionally crystallized from methanol/diethyl ether to yield 85 mg (76%) of 1-methyl-3,3,4,4-tetraphenyl-5-(2,2-diphenylvinyl)-1-cyclopentene (**17**) as colorless plates, mp 170−171 °C.

The spectral characteristics of 1-methyl-3,3,4,4-tetraphenyl-5-(2,2-diphenylvinyl)-1-cyclopentene (**17**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.45−7.02 (m, 20H, arom), 6.91−6.60 (m, 8H, arom), 6.50 (d, 2H, J = 8 Hz, arom), 6.38 (m, 1H, CH═CMe), 5.07 (d, 1H, J = 11.4 Hz, CH═), 4.68 (dm, 1H, J = 11.4 Hz, CH), 1.98 (t, 3H, J = 1.1 Hz, CH_3); UV (hexane) λ-(max) = 258 nm (ϵ = 14 972), λ(shoulder) = 226 nm (ϵ = 22 320); MS *m/e* 564.2808 (calcd for $C_{44}H_{36}$, 564.2817). Anal. Calcd for $C_{44}H_{36}$: C, 93.57; H, 6.43. Found: C, 93.38; H, 6.73. The structure assignment was confirmed by X-ray crystallography (see the Supporting Information).

Kinetics: Direct Solution Photolysis of 3-Methyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (5a). A solution of 10 mg (0.0177 mmol) of 3-methyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**5a**) in 2.5 mL of benzene-d_6 in a NMR tube was irradiated for varying times (see the Supporting Information). The course of the reaction was monitored by ^{1}H NMR spectroscopy.

The spectral characteristics of *cis*-1-methyl-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**15a**) were the following:

^{1}H NMR (benzene-d_6, 300 MHz) δ 7.77−7.69 (m, 2H, arom), 7.56−7.43 (m, 4H, arom), 7.35−7.24 (m, 8H, arom), 7.20−6.80 (m, 16H, arom), 6.68 (s, 1H, CH═), 6.17 (d, 1H, J = 10.7 Hz, CH═), 2.69 (d, 1H, J = 10.7 Hz, CH), 0.90 (s, 3H, CH_3).

The spectral characteristics of *trans*-1-methyl-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**15b**) were the following: ^{1}H NMR (benzene-d_6, 300 MHz) δ 7.50−6.80 (m, 30H, arom), 5.99 (s, 1H, CH═), 5.79 (d, 1H, J = 9.9 Hz, CH═), 2.77 (d, 1H, J = 9.9 Hz, CH), 1.55 (s, 3H, CH_3).

The spectral characteristics of 1-methyl-3,3,4,4-tetraphenyl-5-(2,2-diphenylvinyl)-1-cyclopentene (**17**) were the following: ^{1}H NMR (benzene-d_6, 300 MHz) δ 7.48−7.39 (m, 2H, arom), 7.28−6.65 (m, 28H, arom), 6.31 (dq, 1H, J = 1.5, 1.1 Hz, CH═CMe), 5.34 (d, 1H, J = 11.3 Hz, CH═), 4.92 (ddq, 1H, J = 11.3, 1.5, 1.1 Hz, CH), 1.82 (t, 3H, J = 1.1 Hz, CH_3).

Kinetics: Sensitized (Naphthalene) Solution Photolysis of 3-Methyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (5a). A solution of 10 mg (0.0177 mmol) of 3-methyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**5a**) and 90 mg (0.71 mmol) of naphthalene in 2.5 mL of benzene-d_6 in a NMR tube was irradiated for varying times (see the Supporting Information). The course of the reaction was monitored by ^{1}H NMR spectroscopy.

The spectral characteristics of *cis*- and *trans*-cyclopropanes **15** and cyclopentene **17** were the same as in kinetics direct solution photolysis.

Sensitized (Acetophenone) Solution Photolysis of 3-Methyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (5a). A solution of 150 mg (0.266 mmol) of 3-methyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**5a**) and 5.12 g (42.6 mmol, 4.97 mL) of acetophenone in 200 mL of benzene was irradiated for 10 min. Concentration in vacuo yielded 225 mg of yellow oil. ^{1}H NMR spectroscopic analysis showed 97% conversion and the composition of the reaction mixture was 57% of *cis*-cyclopropane **15a**, 26% of *trans*-cyclopropane **15b** and 14% of cyclopentene **17**. The products were separated by the same way as is described for direct photolysis.

The spectral characteristics of *cis*- and *trans*-cyclopropanes **15** and cyclopentene **17** were the same as in direct solution photolysis.

Kinetics: **Sensitized (Acetophenone) Solution Photolysis of 3-Methyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (5a)**. A solution of 10 mg (0.0177 mmol) of 3-methyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**5a**) and 170 mg (1.42 mmol, 165 μL) of acetophenone in 2.5 mL of benzene-d_6 in a NMR tube was irradiated for varying times (see the Supporting Information). The course of the reaction was monitored by ^{1}H NMR spectroscopy.

The spectral characteristics of *cis*- and *trans*-cyclopropanes **15** and cyclopentene **17** were the same as in exploratory direct solution photolysis.

Solid-State Photolysis of 3-Methyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (5a). A 50 mg (0.088 mmol) portion of crystals of 3-methyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**5a**) was irradiated under conditions described in the General Procedures for 12 h with a Hanovia 450 W medium-pressure mercury lamp. Conversion was 12% and the mixture contained only (as determined by ^{1}H NMR) cyclopropanes **15a**/**15b** in ratio 5:7. The products were separated by the same way as is described for direct photolysis.

The spectral characteristics of *cis*- and *trans*-cyclopropanes **15** were the same as in direct solution photolysis.

Characterization of *cis*-1-Methyl-3,3-diphenyl-1,2-bis-(2,2-diphenylvinyl)cyclopropane (15a).[6,25] A solution of 25 mg (0.044 mmol) of *cis*-1-methyl-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**15a**) in 1.0 mL of benzene was treated with a solution of 100 mg (0.268 mmol) of dicyclohexano-18-crown-6 and 40.2 mg (0.254 mmol) of potassium permanganate in 5.0 mL of benzene and was stirred at room temperature for 80 h and then filtered through Celite. The precipitate was washed with 10% HCl and ether. The filtrate was diluted with ether and after basic workup and concentration in vacuo afforded 115 mg of yellow oil. The oil was chromatographed on a 2 × 50 cm silica gel column eluted with 20% ether in hexane to give 12 mg (75%) of colorless oil which was spectroscopically identical with benzophenone and 27 mg of colorless oil which crystallized from acetone/hexane (1:3) yielding 9.4 mg (72%) of *cis*-1-methyl-3,3-diphenylcyclopropane-1,2-dicarboxylic acid (**16**) as colorless crystals, mp 170−172 °C dec (lit.[6] mp 168−172 °C dec).

The spectral characteristics of *cis*-1-methyl-3,3-diphenylcyclopropane-1,2-dicarboxylic acid (**16**) were the following: ^{1}H NMR (acetone-d_6, 300 MHz) δ 12.5 (bs, 2H, CO_2H), 7.54−7.44 (m, 4H, arom), 7.39−7.30 (m, 2H, arom), 7.28−7.13 (m, 4H, arom), 2.83 (s, 1H, CH), 1.28 (s, 3H, CH_3).

Direct Solution Photolysis of 3-Benzyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (5b). A solution of 150 mg (0.234 mmol) of 3-benzyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**5b**) in 200 mL of benzene was irradiated for 40 min. Concentration in vacuo yielded 160 mg of yellow oil. ^{1}H NMR showed 100% conversion, and the composition of the reaction mixture was 12% of *cis*-cyclopropane **18a**, 6% of *trans*-cyclopropane **18b**, and 82% of cyclopentene **19**. The mixture was crystallized from ethyl acetate/diethyl ether to give 17 mg of a mixture of cis−trans isomers **18**. The rest was fractionally crystallized from acetone/diethyl ether/methanol (1:1:2) to give 96 mg (78%) of 1-benzyl-3,3,4,4-tetraphenyl-5-(2,2-diphenylvinyl)-1-cyclopentene (**19**) as colorless crystals, mp 228−229 °C (at 95−97 °C solvated methanol was lost).

The spectral characteristics of 1-benzyl-3,3,4,4-tetraphenyl-5-(2,2-diphenylvinyl)-1-cyclopentene (**19**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.41−6.92 (m, 29H, arom), 6.80−6.44 (m, 6H, arom), 6.17 (m, 1H, CH═CBz), 5.02 (d, 1H, J = 11.4 Hz, CH═), 4.75 (dm, 1H, J = 11.4 Hz, CH), 3.55 (s, 2H, CH_2Ph); MS *m/e* 640.3139 (calcd for $C_{50}H_{40}$, 640.3130). Anal. Calcd for $C_{51}H_{44}O$: C, 91.03; H, 6.59. Found: C, 91.48; H, 6.37.

Kinetics: Direct Solution Photolysis of 3-Benzyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (5b). A solution of 10 mg (0.0156 mmol) of 3-benzyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**5b**) in 2.5 mL of benzene-d_6 in a NMR tube was irradiated for varying times (see the Supporting Information). The course of the reaction was monitored by ^{1}H NMR spectroscopy.

The spectral characteristics of *cis*-1-benzyl-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**18a**) were the following: ^{1}H NMR (benzene-d_6, 300 MHz) δ 7.60−6.65 (m, 35H, arom), 6.84 (s, 1H, CH═), 6.23 (d, 1H, J = 11 Hz, CH═), 3.02 (d, 1H, J = 11 Hz, CH), 2.50, 2.42 (2 × d, 2H, J = 16.5 Hz, CH_AH_B-Ph).

The spectral characteristics of *trans*-1-benzyl-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**18b**) were the following: ^{1}H NMR (benzene-d_6, 300 MHz) δ 7.58−6.66 (m, 35H, arom), 6.10 (d, 1H, J = 10.3 Hz, CH═), 5.95 (s, 1H, CH═), 3.47, 3.39 (2 × d, 2H, J = 15.4 Hz, CH_AH_BPh), 3.01 (d, 1H, J = 10.3 Hz, CH).

The spectral characteristics of 1-benzyl-3,3,4,4-tetraphenyl-5-(2,2-diphenylvinyl)-1-cyclopentene (**19**) were the following: ^{1}H NMR (benzene-d_6, 300 MHz) δ 7.53−7.49 (m, 2H, arom), 7.32−6.64 (m, 33H, arom), 6.32 (m, 1H, CH═CBz), 5.24 (d, 1H, J = 11.4 Hz, CH═), 5.02 (dm, 1H, J = 11.4 Hz, CH), 3.42 (s, 2H, CH_2Ph).

Kinetics: Sensitized (Naphthalene) Solution Photolysis of 3-Benzyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (5b). A solution of 10 mg (0.0156 mmol) of 3-benzyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**5b**) and 90 mg (0.71 mmol) of naphthalene in 2.5 mL of benzene-d_6 in a NMR tube was irradiated for varying times (see the Supporting Information). The course of the reaction was monitored by ^{1}H NMR spectroscopy.

The spectral characteristics of *cis*- and *trans*-cyclopropanes **18** and cyclopentene **19** were the same as in exploratory direct solution photolysis.

(25) Zimmerman, H. E.; Welter, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 4131−4145.

Sensitized (Acetophenone) Solution Photolysis of 3-Benzyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (5b). A solution of 150 mg (0.234 mmol) of 3-benzyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**5b**) and 5.12 g (42.6 mmol, 4.97 mL) of acetophenone in 200 mL of benzene was irradiated for 5 min. Concentration in vacuo yielded 200 mg of yellow oil. ^{1}H NMR spectroscopic analysis showed 95% conversion, and the composition of the reaction mixture was 52% of *cis*-cyclopropane **18a**, 23% of *trans*-cyclopropane **18b**, and 20% of cyclopentene **19**. The mixture was crystallized from ethyl acetate/ether to give 95 mg of a mixture of cis−trans isomers **18**, then fractional crystallization from acetone/diethyl ether/methanol (1:1:2) afforded 53 mg (68%) of *cis*-1-benzyl-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**18a**) as colorless thin needles, mp 234−235 °C (at 92−93 °C solvated methanol was lost), and 22 mg (63%) of *trans*-1-benzyl-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**18b**) as colorless crystals, mp 220−221 °C (at 91−92 °C solvated methanol was lost).

The spectral characteristics of *cis*-1-benzyl-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**18a**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.57−6.83 (m, 35H, arom), 6.46 (s, 1H, CH═), 5.86 (d, 1H, J = 11 Hz, CH═), 2.68 (d, 1H, J = 11 Hz, CH), 2.27, 2.20 (2 × d, 2H, J = 16.5 Hz, CH_AH_BPh); MS *m/e* 640.3139 (calcd for $C_{50}H_{40}$, 640.3130). Anal. Calcd for $C_{51}H_{44}O$: C, 91.03; H, 6.59. Found: C, 91.50; H, 6.35.

The spectral characteristics of *trans*-1-benzyl-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**18b**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.46−6.79 (m, 35H, arom), 5.72 (s, 1H, CH═), 5.71 (d, 1H, J = 10.3 Hz, CH═), 3.25, 2.79 (2 × d, 2H, J = 15.4 Hz, CH_AH_BPh), 2.75 (d, 1H, J = 10.3 Hz, CH); MS *m/e* 640.3139 (calcd for $C_{50}H_{40}$, 640.3130).

Kinetics: **Sensitized (Acetophenone) Solution Photolysis of 3-Benzyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (5b)**. A solution of 10 mg (0.0156 mmol) of 3-benzyl-3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**5b**) and 170 mg (1.42 mmol, 165 μL) of acetophenone in 2.5 mL of benzene-d_6 in a NMR tube was irradiated for varying times (see the Supporting Information). The course of the reaction was monitored by ^{1}H NMR spectroscopy.

The spectral characteristics of *cis*- and *trans*-cyclopropanes **18** and cyclopentene **19** were the same as in exploratory direct solution photolysis.

Direct Solution Photolysis of 3-(2,2-Diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (3). A solution of 150 mg (0.272 mmol) of 3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**3**) in 200 mL of benzene was irradiated for 15 min. Concentration in vacuo yielded 165 mg of yellow oil. ^{1}H NMR spectroscopic analysis showed 80% conversion and the composition of the reaction mixture was 59% of *cis*-cyclopropane **21a** and 21% of *trans*-cyclopropane **21b**. The starting compound **3** (28 mg) was removed by crystallization of the reaction mixture from benzene/methanol. The filtrate was fractionally crystallized from methanol/dichloromethane to give 64 mg (72%) of *cis*-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**21a**) as colorless thin needles, mp 228−229 °C, and 21 mg (68%) of *trans*-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**21b**) as colorless needles, mp 215−216 °C.

The spectral characteristics of *cis*-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**21a**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.59−6.95 (m, 30H, arom), 5.90 (6 signals[27] of AA′XX′ system, 2H, CH═), 2.57 (6 signals of AA′XX′ system, 2H, CH); MS *m/e* 550.2646 (calcd for $C_{43}H_{34}$, 550.2661). Anal. Calcd for $C_{43}H_{34}$: C, 93.78; H, 6.22. Found: C, 93.81; H, 6.44.

The spectral characteristics of *trans*-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**21b**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.49−6.95 (m, 30H, arom), 5.22 (6 signals[27] of AA′XX′ system, 2H, CH═), 2.59 (6 signals of AA′XX′ system, 2H, CH); MS *m/e* 550.2646 (calcd for $C_{43}H_{34}$, 550.2661).

Kinetics: Direct Solution Photolysis of 3-(2,2-Diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (3). A solution of 10 mg (0.018 mmol) of 3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**3**) in 2.5 mL of benzene-d_6 in a NMR tube was irradiated for varying times. The course of the reaction was monitored by ^{1}H NMR spectroscopy. At the high conversion the secondary photoproduct **22** was spectroscopically observed.

The spectral characteristics of *cis*-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**21a**) were the following: ^{1}H NMR (benzene-d_6, 300 MHz) δ 7.72 (m, 2H, arom), 7.53−6.75 (m, 28H, arom), 6.34 (6 signals[27] of AA′XX′ system, 2H, CH═), 2.87 (6 signals of AA′XX′ system, 2H, CH).

The spectral characteristics of *trans*-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**21b**) were the following: ^{1}H NMR (benzene-d_6, 300 MHz) δ 7.51−6.73 (m, 30H, arom), 5.53 (6 signals[27] of AA′XX′ system, 2H, CH═), 2.99 (6 signals of AA′XX′ system, 2H, CH).

Kinetics: **Sensitized (Naphthalene) Solution Photolysis of 3-(2,2-Diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (3).** A solution of 10 mg (0.018 mmol) of 3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**3**) and 90 mg (0.71 mmol) of naphthalene in 2.5 mL of benzene-d_6 in a NMR tube was irradiated for varying times. The course of the reaction was monitored by ^{1}H NMR spectroscopy.

The spectral characteristics of *cis*- and *trans*-cyclopropanes **21** were the same as in exploratory direct solution photolysis.

Sensitized (Acetophenone) Solution Photolysis of 3-(2,2-Diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (3). A solution of 150 mg (0.272 mmol) of 3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**3**) and 5.12 g (42.6 mmol, 4.97 mL) of acetophenone in 200 mL of benzene was irradiated for 8 min. Concentration in vacuo yielded 200 mg of yellow oil. ^{1}H NMR spectroscopic analysis showed 100% conversion and the composition of the reaction mixture was 55% of *cis*-cyclopropane **21a** and 45% of trans-cyclopropane **21b**. Fractional crystallization from methanol/dichloromethane gave 54 mg (65%) of *cis*-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)-cyclopropane (**21a**) as colorless thin needles, mp 228−229 °C, and 37 mg (55%) of *trans*-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**21b**) as colorless crystals, mp 215−216 °C.

The spectral characteristics of *cis*- and *trans*-cyclopropanes **21** were the same as in direct solution photolysis.

Kinetics: Sensitized (Acetophenone) Solution Photolysis of 3-(2,2-Diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (3). A solution of 10 mg (0.018 mmol) of 3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**3**) and 170 mg (1.42 mmol, 165 μL) of acetophenone in 2.5 mL of benzene-d_6 in a NMR tube was irradiated for varying times. The course of the reaction was monitored by ^{1}H NMR spectroscopy.

The spectral characteristics of *cis*- and *trans*-cyclopropanes **21** were the same as in exploratory direct solution photolysis.

Solid-State Photolysis of 3-(2,2-Diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (3). A 50 mg (0.091 mmol) portion of crystals of 3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**3**) was irradiated under conditions described in the General Procedures for 12 h with a Hanovia 450 W medium-pressure mercury lamp. Conversion was 8% and the mixture contained (as determined by ^{1}H NMR) cyclopropanes **21a**/**21b** in ratio 5/6. The products were separated by the same way as is described for direct photolysis.

The spectral characteristics of *cis*- and *trans*-cyclopropanes **21** were the same as in direct solution photolysis.

Characterization of *cis*-3,3-Diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (21a).[25,26] A solution of 25 mg (0.045 mmol) of *cis*-3,3-diphenyl-1,2-bis(2,2-diphenylvinyl)cyclopropane (**21a**) in 1.0 mL of benzene was treated with a solution of 100 mg (0.268 mmol) of dicyclohexano-18-crown-6 and 40.2 mg (0.254 mmol) of potassium permanganate in 5.0 mL of benzene, stirred at room temperature for 70 h, and then filtered through Celite. The precipitate was washed with 10% HCl and ether. The filtrate was diluted with ether and after basic workup and concentration in vacuo was obtained 123 mg of yellow oil. The oil was chromatographed on a 2 × 50 cm silica gel column eluted with 15% ether in hexane and gave 11 mg (67%) of colorless oil which was spectroscopically identical with benzophenone and 22 mg of colorless oil which

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(27) Günther, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 861−874.

crystallized from acetone/water (3:1) yielding 8.3 mg (65%) of *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid as colorless crystals, mp 203−205 °C dec (lit.[26] mp 204−206 °C dec).

The spectral characteristics of *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid were the following: ^{1}H NMR (acetone-d_6, 300 MHz) δ 11.3 (bs, 2H, CO_2H), 7.51−7.43 (m, 4H, arom), 7.36−7.19 (m, 6H, arom), 2.94 (s, 2H, CH).

Direct Solution Photolysis of Methyl 2-Carbomethoxy-4-methyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate (14a). A solution of 200 mg (0.378 mmol) of methyl 2-carbomethoxy-4-methyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate (**14a**) in 200 mL of benzene was irradiated for 10 min. Concentration in vacuo yielded 215 mg of an orange oil. ^{1}H NMR spectroscopic analysis showed 100% conversion and suggested four compounds, 34% of **25a**, 20% of **24a**, 23% of **23a trans**, and 23% of **23a cis**. The mixture was separated on a preparative silica gel TLC plate eluted with 25% of diethyl ether in hexane. Band 1 contained 65 mg of 1,1,4,4-tetraphenyl-1,3-butadiene as white crystals, mp 201−203 °C (lit.[28] mp 203 °C). Band 2 gave 25 mg (54%) of *cis*-1,1-diphenyl-2-methyl-2-(2,2-dicarbomethoxyvinyl)-3-(2,2-diphenylvinyl)cyclopropane (**23a cis**) as a viscous oil, band 3 gave 22 mg (48%) of *trans*-1,1-diphenyl-2-methyl-2-(2,2-dicarbomethoxyvinyl)-3-(2,2-diphenylvinyl)cyclopropane (**23a trans**) as a viscous oil, band 4 gave 20 mg (50%) of 1,1-diphenyl-2-methyl-2-(2,2-diphenylvinyl)-3-(2,2-dicarbomethoxyvinyl)cyclopropane (**24a**) as an oil and band 5 contained 42 mg (62%) of 1,1-dicarbomethoxy-2-methyl-2,3-bis(2,2-diphenylvinyl)cyclopropane (**25a**) as a yellow viscous oil.

The spectral characteristics of 1,1-dicarbomethoxy-2-methyl-2,3-bis(2,2-diphenylvinyl)cyclopropane (**25a**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.52−6.82 (m, 20H, arom), 6.32 (s, 1H, CH=CPh), 5.73 (d, 1H, J = 8 Hz, CH=CPh), 3.88 and 3.64 (2 × s, 6H, CH_3OCO), 2.75 (d, 1H, J = 8 Hz, CH), 1.37 (s, 3H, CH_3); MS *m/e* 528.2305 (calcd for $C_{36}H_{32}O_4$, 528.2301).

The spectral characteristics of 1,1-diphenyl-2-methyl-2-(2,2-diphenylvinyl)-3-(2,2-dicarbomethoxyvinyl)cyclopropane (**24a**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.53−6.85 (m, 21H, arom and CH=CCO), 5.89 (s, 1H, CH=CPh), 3.71, 3.70 (2 × s, 6H, CH_3OCO), 2.42 (d, 1H, J = 8 Hz, CH), 1.26 (s, 3H, CH_3); MS *m/e* 528.2303 (calcd for $C_{36}H_{32}O_4$, 528.2301).

The spectral characteristics of *trans*-1,1-diphenyl-2-methyl-2-(2,2-dicarbomethoxyvinyl)-3-(2,2-diphenylvinyl)cyclopropane (**23a-trans**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55−6.90 (m, 20H, arom), 6.42 (s, 1H, CH=CCO), 5.97 (d, 1H, J = 9.5 Hz, CH=CPh), 3.76 and 3.67 (2 × s, 6H, CH_3OCO), 2.53 (d, 1H, J = 9.5 Hz, CH), 0.99 (s, 3H, CH_3); MS *m/e* 528.2305 (calcd for $C_{36}H_{32}O_4$, 528.2301).

The spectral characteristics of *cis*-1,1-diphenyl-2-methyl-2-(2,2-dicarbomethoxyvinyl)-3-(2,2-diphenylvinyl)cyclopropane (**23a-cis**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.54−6.83 (m, 21H, arom and CH=CCO), 6.02 (d, 1H, J = 9.5 Hz, CH=CPh), 3.89 and 3.71 (2 × s, 6H, CH_3OCO), 2.54 (d, 1H, J = 9.5 Hz, CH), 0.98 (s, 3H, CH_3); MS *m/e* 528.2303 (calcd for $C_{36}H_{32}O_4$, 528.2301).

Sensitized Solution Photolysis of Methyl 2-Carbomethoxy-4-methyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate (14a). A solution of 100 mg (0.189 mmol) of methyl 2-carbomethoxy-4-methyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate (**14a**) and 3.44 g (28.6 mmol) of acetophenone in 200 mL of benzene was irradiated for 15 min. Concentration in vacuo yielded 150 mg of an orange-brown oil. The mixture was separated on a preparative silica gel TLC plate eluted with 15% diethyl ether in hexane. Band 1 afforded 15 mg of 1,1,4,4-tetraphenyl-1,3-butadiene. Band 2 gave 55 mg (55%) of a viscous oil. ^{1}H NMR analysis suggested a cyclopentene product. Crystallization from methanol/ether (2:1) yielded 33 mg (33%) of 1-methyl-3,3,5,5-tetraphenyl-4-(2,2-dicarbomethoxyvinyl)-1-cyclopentene (**26a**) as white crystals, mp 152−157 °C. Band 3 contained 10 mg (10%) of the mixture of cyclopropanes **23a**−**25a**, and band 4 included 45 mg of the rest of sensitizer.

The spectral characteristics of 1-methyl-3,3,5,5-tetraphenyl-4-(2,2-dicarbomethoxyvinyl)-1-cyclopentene (**26a**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.52−7.00 (m, 20H, arom), 6.25 (q, 1H, J = 1.5 Hz, CH=CMe), 5.88 (d, 1H, J = 12 Hz, CH=CCO), 5.11 (d, 1H, J = 12 Hz, CH), 3.54 and 3.38 (2 × s, 6H, CH_3OCO), 1.57 (d, 3H, J = 1.5 Hz, CH_3); ^{1}H NMR (benzene-d_6, 300 MHz) δ 7.78−7.72 (m, 2H, arom), 7.42−6.82 (m, 18H, arom), 6.25 (d, 1H, J = 11.8 Hz, CH=CCO), 6.10 (q, 1H, J = 1.1 Hz, CH=CMe), 5.51 (d, 1H, J = 11.8 Hz, CH), 3.18, 3.12 (2 × s, 6H, CH_3OCO), 1.49 (d, 3H, J = 1.1 Hz, CH_3); MS *m/e* 528.2327 (calcd for $C_{36}H_{32}O_4$, 528.2301). Anal. Calcd for $C_{36}H_{32}O_4$: C, 81.79; H, 6.10. Found: C, 81.47; H, 6.22. The structure assignment was confirmed by X-ray crystallography (see the Supporting Information).

Direct Solution Photolysis of Methyl 2-Carbomethoxy-4-benzyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate (14b). A solution of 200 mg (0.331 mmol) of methyl 2-carbomethoxy-4-benzyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate (**14b**) in 200 mL of benzene was irradiated for 8 min. Concentration in vacuo yielded 220 mg of an orange oil. ^{1}H NMR spectroscopic analysis showed 100% conversion and suggested four components, 44% of **25b**, 18% of **24b**, 18% of **23b-trans**, and 20% of **23b-cis**. The mixture was separated on a preparative silica gel TLC plate eluted with 20% of diethyl ether in hexane. Band 1 contained 45 mg of 1,1,4,4-tetraphenyl-1,3-butadiene as white crystals, mp 201−203 °C (lit.[28] mp 203 °C). Band 2 gave 27 mg (67%) of *cis*-1,1-diphenyl-2-benzyl-2-(2,2-dicarbomethoxyvinyl)-3-(2,2-diphenylvinyl)cyclopropane (**23b-cis**) as a viscous oil, band 3 gave 23 mg (64%) of *trans*-1,1-diphenyl-2-benzyl-2-(2,2-dicarbomethoxyvinyl)-3-(2,2-diphenylvinyl)cyclopropane (**23b-trans**) as a viscous oil, band 4 gave 18 mg (50%) of 1,1-diphenyl-2-benzyl-2-(2,2-diphenylvinyl)-3-(2,2-dicarbomethoxyvinyl)cyclopropane (**24b**) as an oil, and band 5 contained 56 mg (64%) of 1,1-dicarbomethoxy-2-benzyl-2,3-bis(2,2-diphenylvinyl)cyclopropane (**25b**) as a viscous oil.

The spectral characteristics of 1,1-dicarbomethoxy-2-benzyl-2,3-bis(2,2-diphenylvinyl)cyclopropane (**25b**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.48−6.81 (m, 25H, arom), 5.92 (s, 1H, CH=CPh), 5.78 (d, 1H, J = 10 Hz, CH=CPh), 3.31 and 3.08 (2 × s, 6H, CH_3OCO), 3.07 (m, 2H, CH_2Ph), 2.77 (d, 1H, J = 10 Hz, CH); MS *m/e* 604.2610 (calcd for $C_{42}H_{36}O_4$, 604.2614). Anal. Calcd for $C_{42}H_{36}O_4$: C, 83.42; H, 6.00. Found: C, 83.61; H, 6.09.

The spectral characteristics of 1,1-diphenyl-2-benzyl-2-(2,2-diphenylvinyl)-3-(2,2-dicarbomethoxyvinyl)cyclopropane (**24b**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.42−6.85 (m, 26H, arom and CH=CCO), 5.87 (s, 1H, CH=CPh), 3.78 and 3.72 (2 × s, 6H, CH_3OCO), 3.48 (m, 2H, CH_2Ph), 2.46 (d, 1H, J = 9 Hz, CH); MS *m/e* 604.2609 (calcd for $C_{42}H_{36}O_4$, 604.2614). Anal. Calcd for $C_{42}H_{36}O_4$: C, 83.42; H, 6.00. Found: C, 83.25; H, 5.99.

The spectral characteristics of *trans*-1,1-diphenyl-2-benzyl-2-(2,2-dicarbomethoxyvinyl)-3-(2,2-diphenylvinyl)cyclopropane (**23b-trans**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.54−6.89 (m, 25H, arom), 6.27 (s, 1H, CH=CCO), 5.88 (d, 1H, J = 10 Hz, CH=CPh), 3.81 and 3.63 (2 × s, 6H, CH_3OCO), 3.17 (m, 2H, CH_2Ph), 2.59 (d, 1H, J = 10 Hz, CH); MS *m/e* 604.2610 (calcd for $C_{42}H_{36}O_4$, 604.2614).

The spectral characteristics of *cis*-1,1-diphenyl-2-benzyl-2-(2,2-dicarbomethoxyvinyl)-3-(2,2-diphenylvinyl)cyclopropane (**23b-cis**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55−6.88 (m, 26H, arom and CH=CCO), 5.95 (d, 1H, J = 11 Hz, CH=CPh), 3.88 and 3.73 (2 × s, 6H, CH_3OCO), 3.31 (m, 2H, CH_2Ph), 2.51 (d, 1H, J = 11 Hz, CH); MS *m/e* 604.2609 (calcd for $C_{42}H_{36}O_4$, 604.2614). Anal. Calcd for $C_{42}H_{36}O_4$: C, 83.42; H, 6.00. Found: C, 83.49; H, 5.91.

Sensitized Solution Photolysis of Methyl 2-Carbomethoxy-4-benzyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate (14b). A solution of 100 mg (0.165 mmol) of methyl 2-carbomethoxy-4-benzyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate (**14b**) and 3.44 g (28.6 mmol) of acetophenone in 200 mL of benzene was irradiated for 15 min.

(28) Sasaki, K.; Nakao, K.; Kobayashi, Y.; Sakai, M.; Uchino, N.; Sakakibara, Y.; Takagi, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2446−2448.

Concentration in vacuo yielded 185 mg of an orange oil. The mixture was separated on a preparative silica gel TLC plate eluted with 10% diethyl ether in hexane. Band 1 contained 13 mg of 1,1,4,4-tetraphenyl-1,3-butadiene. Band 2 gave 66 mg (66%) of a yellow oil. ^{1}H NMR analysis suggested a cyclopentene product. Crystallization from acetone/ether/methanol (1:1:2) yielded 43 mg (43%) of-1-benzyl-3,3,5,5,-tetraphenyl-4-(2,2-dicarbomethoxyvinyl-1-cyclopentene (**26b**) as white crystals, mp 203−204 °C. Band 3 contained 14 mg (14%) of the mixture of cyclopropanes **23b**−**25b**, and band 4 included 55 mg of the rest of sensitizer.

The spectral characteristics of 1-benzyl-3,3,5,5-tetraphenyl-4-(2,2-dicarbomethoxyvinyl)-1-cyclopentene (**26b**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40−6.82 (m, 25H, arom), 5.90 (d, 1H, J = 11.4 Hz, CH=CCO), 5.87 (m, 1H, CH=CBz), 5.15 (d, 1H, J = 11.4 Hz, CH), 3.53, 3.37 (2 × s, 6H, CH_3OCO), 3.33, 2.69 (2 × dd, 2H, J = 16.9, 1.5 Hz, CH_AH_B-Ph); ^{1}H NMR (benzene-d_6, 300 MHz) δ 7.67−7.54 (m, 4H, arom), 7.52−7.45 (m, 2H, arom), 7.30−6.76 (m, 19H, arom), 6.29 (d, 1H, J = 11.8 Hz, CH=CCO), 6.10 (dd, 1H, J = 1.5, 1.1 Hz, CH=CBz), 5.60 (d, 1H, J = 11.8 Hz, CH), 3.28 (dd, 1H, J = 17, 1.5 Hz, CH_2Ph), 3.20, 3.13 (2 × s, 6H, CH_3OCO), 2.80 (dd, 1H, J = 17, 1.1 Hz, CH_2Ph); MS *m/e* 604.2609 (calcd for $C_{42}H_{36}O_4$, 604.2614). Anal. Calcd for $C_{42}H_{36}O_4$: C, 83.42; H, 6.00. Found: C, 83.53; H, 6.02.

Solid-State Photolysis of Methyl 2-Carbomethoxy-4-benzyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate (14b). A 50 mg (0.083 mmol) portion of crystals of methyl 2-carbomethoxy-4-benzyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate (**14b**) was irradiated under conditions described in the General Procedures for 10 h with a Hanovia 450 W medium-pressure mercury lamp. The reaction mixture contained only starting compound (after the analysis with ^{1}H NMR).

Sensitized Solution Photolysis of 2-Cyano-4-methyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienenitrile (27).[5a] A solution of 100 mg (0.216 mmol) of 2-cyano-4-methyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienenitrile (**27**) and 3.4 g (28.6 mmol) of acetophenone in 200 mL of benzene was irradiated for 2 h. Concentration in vacuo yielded 155 mg of pale yellow oil. Chromatography of the crude material on a 3 × 15 cm silica gel column eluted with 20% ether in hexane gave 50 mg of yellow oil which was crystallized from methanol/dichloromethane (3:1) to give 45 mg (45%) of 1-methyl-3,3,5,5-tetraphenyl-4-(2,2-dicyanovinyl)-1-cyclopentene (**29**) as white needles, mp 206−208 °C.

The spectral characteristics of 1-methyl-3,3,5,5-tetraphenyl-4-(2,2-dicyanovinyl)-1-cyclopentene (**29**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.51−7.38 (m, 4H, arom), 7.37−7.03 (m, 16H, arom), 6.21 (q, 1H, J = 1.5 Hz, CH=CMe), 6.01 (d, 1H, J = 12 Hz, CH=CCN), 5.33 (d, 1H, J = 12 Hz, CH), 1.65 (d, 3H, J = 1.5 Hz, CH_3); ^{1}H NMR (benzene-d_6, 300 MHz) δ 7.51 (m, 4H, arom), 7.35−6.74 (m, 16H, arom), 5.92 (d, 1H, J = 12.1 Hz, CH=CCN), 5.86 (q, 1H, J = 1.5 Hz, CH=CMe), 5.61 (d, 1H, J = 12.1 Hz, CH), 1.40 (d, 3H, J = 1.5 Hz, CH_3); MS *m/e* 462.2103 (calcd for $C_{34}H_{26}N_2$, 462.2095).

1-Methyl-3,3-diphenyl-4,4-dicarbomethoxy-5-(2,2-diphenylvinyl)-1-cyclopentene (30a). ($TiCl_4$ method) To 3.0 mL of anhyd THF at 0 °C was added 89 mg (0.47 mmol, 52 μL) of titanium tetrachloride[24] in 0.125 mL of tetrachloromethane. To this yellow mixture was added 100 mg (0.189 mmol) of methyl 2-carbomethoxy-4-methyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate (**14a**) in 0.50 mL of anhyd THF. The mixture was stirred at 0 °C for 20 min followed by addition of 79 mg (1.0 mmol, 81 μL) of anhyd pyridine. The yellow solution was allowed to warm to room temperature, followed by addition of 3.4 mg (0.189 mmol, 3.4 μL) of water and stirred an additional 24 h. The crude reaction mixture was filtered through a 0.5 × 2 cm silica gel column eluted with ether, dried and concentrated in vacuo leaving 0.11 g of yellow oil. Chromatography of the crude product on a 3 × 20 cm silica gel column eluted with 30% ether in hexane gave 100 mg of yellow oil which was crystallized from ether/methanol (1:2) to afford 85 mg (81%) of 1-methyl-3,3-diphenyl-4,4-dicarbomethoxy-5-(2,2-diphenylvinyl)-1-cyclopentene (**30a**) as colorless crystals, mp 175−177 °C.

The spectral characteristics were the following: ^{1}H NMR (benzene-d_6, 300 MHz) δ 7.98−7.85 (m, 2H, arom), 7.51−6.75 (m, 18H, arom), 6.21 (d, 1H, J = 10.6 Hz, CH=CPh), 5.88 (m, 1H, CH=CMe), 5.14 (dm, 1H, J = 10.6 Hz, CH), 3.05 and 2.99 (2 × s, 6H, CH_3OCO), 1.85 (bs, 3H, CH_3); UV (hexane) λ(max) = 254 nm (ϵ = 17 140), λ(shoulder) = 226 nm (ϵ = 18 090), λ = 300 nm (ϵ = 2); MS *m/e* 528.2315 (calcd for $C_{36}H_{32}O_4$, 528.2301). Anal. Calcd for $C_{36}H_{32}O_4$: C, 81.79; H, 6.10. Found: C, 82.16; H, 6.12. The structure assignment was confirmed by X-ray crystallography (see the Supporting Information).

1-Methyl-3,3-diphenyl-4,4-dicarbomethoxy-5-(2,2-diphenylvinyl)-1-cyclopentene (30a) (BF_3·Et_2O Method). To 3.0 mL of anhyd diethyl ether was added 28 mg (0.20 mmol) of boron trifluoride etherate and then 106 mg (0.20 mmol) of methyl 2-carbomethoxy-4-methyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate (**14a**) in 1.0 mL of anhyd ether. The mixture was stirred at room temperature for 24 h. The crude reaction mixture was filtered through a 0.5 × 2 cm plug of silica gel eluted with ether, dried and concentrated in vacuo leaving 95 mg of yellow oil. Chromatography of the crude product on a 3 × 15 cm silica gel column eluted with 30% ether in hexane gave 90 mg of yellow oil which was crystallized from ether/methanol (1:2) to afford 80 mg (76%) of 1-methyl-3,3-diphenyl-4,4-dicarbomethoxy-5-(2,2-diphenylvinyl)-1-cyclopentene (**30a**) as colorless crystals, mp 175−177 °C, identical with material obtained from the $TiCl_4$ method (vide supra).

1-Benzyl-3,3-diphenyl-4,4-dicarbomethoxy-5-(2,2-diphenylvinyl)-1-cyclopentene (30b). To 3.0 mL of anhyd diethyl ether was added 28 mg (0.20 mmol) of boron trifluoride etherate and then 121 mg (0.20 mmol) of methyl 2-carbomethoxy-4-benzyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate (**14b**) in 1.0 mL of anhyd ether. The mixture was stirred at room temperature for 24 h. The crude reaction mixture was filtered through a 0.5 × 2 cm plug of silica gel eluted with ether, dried and concentrated in vacuo leaving 110 mg of oil. Chromatography of the crude product on a 3 × 15 cm silica gel column eluted with 30% ether in hexane gave 105 mg of yellow oil which was crystallized from ether/methanol (1:2) to afford 98 mg (81%) of 1-benzyl-3,3-diphenyl-4,4-dicarbomethoxy-5-(2,2-diphenylvinyl)-1-cyclopentene (**30b**) as colorless crystals, mp 226−228 °C.

The spectral characteristics were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.70−7.55 (d, 2H, J = 7 Hz, arom), 7.53−7.15 (m, 18H, arom), 7.05−6.93 (m, 3H, arom), 6.90−6.73 (m, 2H, arom), 6.50 (dt, 1H, J = 2.6, 2.0 Hz, CH=CBz), 5.62 (d, 1H, J = 10 Hz, CH=CPh), 4.81 (ddt, 1H, J = 10, 2.6, 2.0 Hz, CH), 3.95 (m, 2H, CH_2Ph), 3.77 and 2.89 (2 × s, 6H, CH_3OCO); MS *m/e* 604.2609 (calcd for $C_{42}H_{36}O_4$, 604.2614). Anal. Calcd for $C_{42}H_{36}O_4$: C, 83.42; H, 6.00. Found: C, 83.76; H, 6.09.

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Supporting Information Available: Programming details and further kinetic results are given. This material is available free of charge via the Internet at http://pubs.acs.org.

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