with a flame-ionization detector. Analysis of the parent solution gave values for 1, the sum of 6 and 7, 11, 8, tetralin, and 1-tetralol (?). In runs containing benzophenone, the formation of diphenylmethane was also monitored. Analysis after base extraction to remove all phenolic components gave the most reliable value for 6. Analysis after trimethylsilylation gave values for 2 and 12 and the most reliable value for 7. The binaphthols were detected only after trimethylsilylation because they apparently react with the Dexsil stationary phase before eluting. All peak areas were determined with a planimeter and were converted to molar amounts on the basis of an internal standard and calibration factors determined with authentic samples.

A similar procedure was used for 2-N thermolyses except that acetone was used as solvent. The base-extraction step was omitted and acetone was gently evaporated from an aliquot before trimethylsilylation. GC analyses were performed on an OV-101 WCOT column, temperature programmed from 75 to 280 °C at 12 °C/min. Direct analysis gave values for all products except the binaphthols, which were determined after trimethylsilylation. Peak areas were determined by electronic integration.

Occasional checks for formation of noncondensable gas were made. The reaction tube, before opening, was attached with plastic tubing to a manometer and the closed system was evacuated. With the lower portion of the tube cooled in dry ice–acetone, the tip was crushed through the plastic tubing. No significant increases in pressure were noted. For occasional measurements of water formation, reaction mixtures were dissolved in dioxane containing 2-propanol as an internal standard. GC analysis for water and 2-propanol was performed on a Poropak Q column with a thermal conductivity detector.

Acknowledgment. Some initial exploratory experiments were successfully performed by Martin Sahler, Oak Ridge Associated Universities Summer Research Participant.

Registry No. 1, 831-82-3; 2, 604-60-4; 3, 239-69-0; 4, 602-09-5; 5, 204-91-1; 6, 604-60-4; 7, 529-35-1; 8, 91-20-3; 9, 119-64-2; 10, 529-33-9; 11, 607-52-3; 12, 1446-34-0; 13, 613-80-9; 14, 530-93-8; 15, 1125-78-6; 16, 82495-18-9; Ph_2CH_2, 103-29-7; benzophenone, 119-61-9; 1,1'-Dioxo-4,4'-bis[2,5-cyclohexadiene], 82495-19-0; 4'-hydroxy-4-phenyl-2,5-cyclohexidien-1-one, 82495-20-3; 1,1'-biphenyl-4,4'-diol, 2122-46-5; 4-phenoxyphenol, 831-82-3; 4-phenoxy-2,5-cyclohexadien-1-one, 82495-21-4.

Cyclopropene Photochemistry. Mechanistic and Exploratory Organic Photochemistry[1,2]

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Received September 21, 1981

Four new cyclopropenes have been synthesized and their photochemistry has been investigated. Thus, 3-methyl-1,2-diphenyl-3-(2-phenylallyl)cyclopropene was found on direct photolysis to afford four photoproducts, the two major products of which derived from novel photochemistry. 2-Methylene-4-methyl-5,6-diphenyltetracyclo[5.4.0.0.^{1,5}0^{4,6}]undeca-8,10-diene derived from [2 + 2] cycloaddition of the excited cyclopropenyl π bond to the C-1,C-2 π bond of the phenyl of the 2-phenylallyl side chain. The quantum yield for this novel transformation was 0.023. A second photoproduct was 2-methyl-1,4,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane. This product results from a formal [2 + 2] cycloaddition of the excited cyclopropenyl π bond to the allyl double bond. A diradical mechanism is structurally equivalent. Formation of such a tricyclic [2.2.0.0^{2,6}] system is normally not found in direct irradiations. The quantum yield for this product was 0.088. Also formed was 3-methyl-1,2,5-triphenylbicyclo[3.1.0]hex-2-ene with an efficiency of 0.019. This product is understood as deriving either (i) from cyclopropene opening to a carbene which then adds to the allyl π bond or (ii) from a bicyclic diradical arising from vinyl–vinyl bonding. The fourth photoproduct is 2-methyl-1,3-diphenyl-3-(2-phenylallyl)cyclopropene. The efficiency was 0.018. The bicyclic diradical above provides a common species leading to the last three products. Sensitization led only to the first two products: the tetracyclic diene (ϕ = 0.26) and the tricyclo[2.2.0.0^{2,6}]hexane (ϕ = 0.15). Product structures were established by X-ray, degradation, independent synthesis, and spectral analysis. In addition, the photochemistry of *cis*- and *trans*-2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene was investigated. Stereoisomerization resulted from the singlet but not the triplet. Mechanisms for the above transformations are considered. Finally, corresponding thermal chemistry exhibited by the above compounds was investigated.

Introduction

In our previous studies,[2b,3] we reported the photochemical transformation of vinylcyclopropenes to afford cyclopentadienes. Similarly, Padwa[4,5] has investigated the photochemical behavior of vinyl[4] and allyl[5] cyclopropenes. Cyclopropene photochemistry has been unusual in the rich variety of different types of photochemical transformations encountered.

Our present research began with an investigation of the photochemistry of 3-methyl-1,2-diphenyl-3-(2-phenylallyl)cyclopropene (1). Additionally, the photochemistry

(1) (a) This is paper 134 of our photochemical series. (b) It is paper 5 of our series on "Cyclopropene Photochemistry". See ref 2f for our last paper on cyclopropene chemistry.

(2) (a) For paper 129, note Zimmerman, H. E. *Tetrahedron* **1982**, *38*, 753–758. (b) For an earlier publication on cyclopropene chemistry, see Zimmerman, H. E.; Hovey, M. C. *J. Org. Chem.* **1979**, *44*, 2331–2345. (c) Publication 130: Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; deMayo, P., Ed.; Academic Press: New York, 1980; Chapter 16. (d) Paper 131: Zimmerman, H. E.; Penn, J. H.; Carpenter, C. W. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 2128–2132. (e) Publication 132: Zimmerman, H. E. *Top. Curr. Chem.* **1982**, *100*, 45–73. (f) Paper 133: Zimmerman, H. E.; Kreil, D. J. *J. Org. Chem.* **1982**, *47*, 2060–2075.

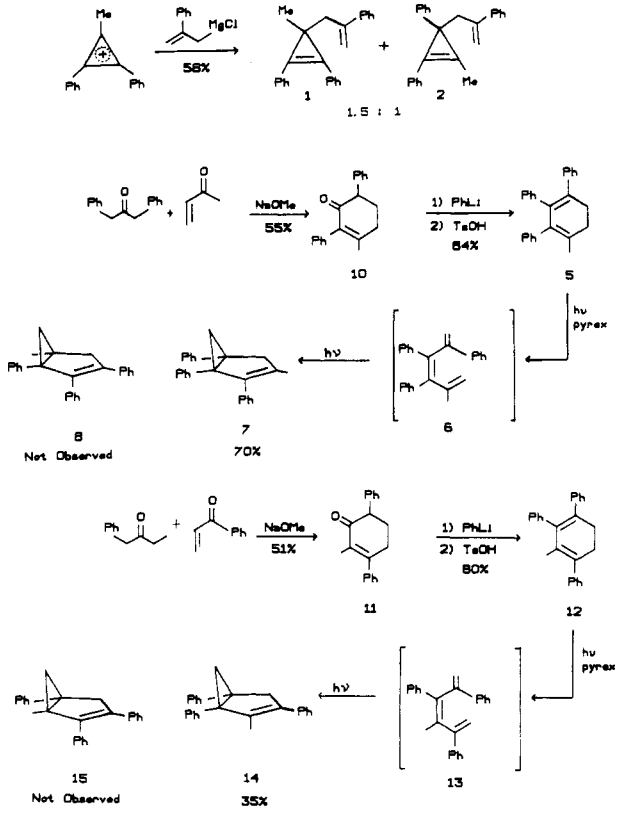
(3) (a) Zimmerman, H. E.; Aasen, S. M. *J. Am. Chem. Soc.* **1977**, *99*, 2342–2344. (b) Zimmerman, H. E.; Aasen, S. M. *J. Org. Chem.* **1978**, *43*, 1493–1506.

(4) (a) Padwa, A.; Blacklock, T. J.; Getman, D.; Hatanaka, N. *J. Am. Chem. Soc.* **1977**, *99*, 2344–2345. (b) *J. Org. Chem.* **1978**, *43*, 1481–1492. (c) For a general review of more recent papers by these authors, note Padwa, A. *Org. Photochem.* **1979**, *4*, 261–326.

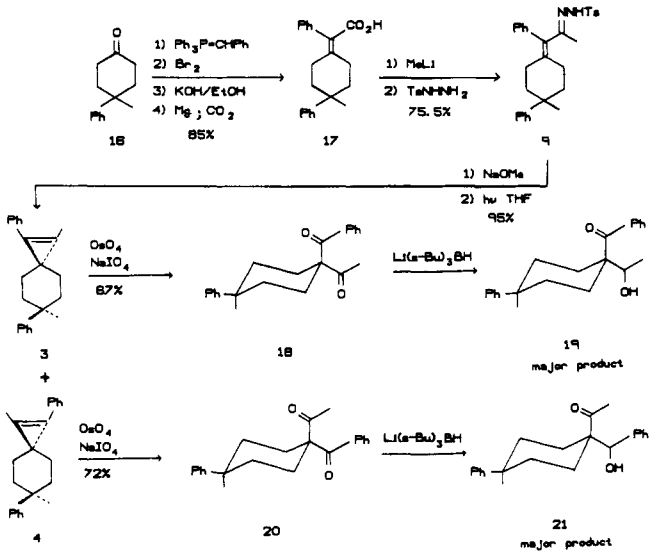
(5) (a) Padwa, A.; Blacklock, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2345–2347. (b) For a very recent paper with references to intervening literature, see Padwa, A.; Blacklock, T. J.; Cordova, D. M.; Loza, R. *Ibid.* **1980**, *102*, 5648–5656.

0022-3263/82/1947-3377$01.25/0

Scheme I. Syntheses of (Phenylallyl)cyclopropene Photoreactants and Potential Photoproducts



Scheme II. Synthesis of Spirocyclopropenes and Stereochemical Assignments



of 2-methyl-1,3-diphenyl-3-(2-phenylallyl)cyclopropropene (**2**) was studied. Finally, to determine behavior of the cyclopropene ring in the absence of the allyl side chain, the photochemistry of the cis and trans isomers of 2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene (**3**, **4**) was investigated.

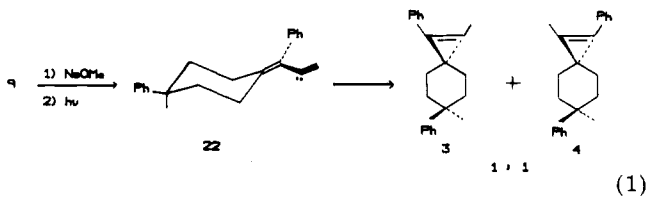
Results

Synthesis of Photochemical Reactants and Potential Photoproducts. The synthesis of the (phenylallyl)cyclopropene reactants is outlined in Scheme I. Also included are some syntheses of compounds encountered in the photochemistry of these compounds. The synthesis of the spirocyclopropenes **3** and **4** is depicted in Scheme II.

The stereochemistry of the spirocyclopropenes **3** and **4** was assigned chemically. Thus, osmium tetraoxide/sodium metaperiodate oxidation led to the corresponding cis and trans diketones **18** and **20** as in Scheme II. Then partial lithium tri-*sec*-butylborohydride reduction, giving preferential equatorial carbonyl reduction, allowed determination of whether the phenyl- or methyl-bearing carbonyl group was equatorial (note Experimental Section).

Several aspects of the syntheses are of particular interest and invite comment. One is the photochemical synthesis of 3-methyl-1,2,5-triphenylbicyclo[3.1.0]hex-2-ene (**7**) from 4-methyl-1,2,3-triphenyl-1,3-cyclohexadiene (**5**), most reasonably formulated as proceeding via 5-methyl-2,3,4-triphenyl-1,3,5-hexatriene (**6**). A priori, closure of the triene could lead either to the desired bicyclo[3.1.0]hexene **7** or to its regioisomer 5-methyl-1,2,3-triphenylbicyclo-[3.1.0]hex-2-ene (**8**).

Another item of real interest was the high-yield conversion of tosylhydrazone **9** to the isomeric spirocyclopropenes **3** and **4**. There were formed in a 1:1 ratio, despite the reactions involving an axial carbene attack on the six ring in one case and an equatorial attack in the other. This is depicted in eq 1.



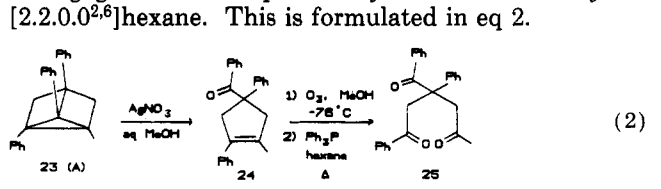
(1)

Exploratory Photochemistry of the (Phenylallyl)-cyclopropenes and Structure Elucidation of the Photoproducts. Direct photolysis of the 3-methyl-3-(phenylallyl)cyclopropene **1** was found to afford four photoproducts: A, B, C, and D in a ratio of 4:1:1:1.

$$1 \xrightarrow[h\nu]{} A + B + C + D$$

Photoproduct A showed no vinyl absorption in the NMR spectrum. A single, unsplit methyl peak appeared at δ 1.42. Additionally, there were two independent AB quartets, centered at δ 2.70 and 2.93, typical of CH_2 groups. Carbon-13 NMR indicated the presence of seven aliphatic carbons in addition to aromatic carbons. The ultraviolet spectrum showed only unconjugated phenyl groups to be present. Bromination of photoproduct A, followed by basic alumina chromatography afforded 2,3,5-triphenyltoluene, thus partially defining the molecular connectivity.

Treatment of photoproduct A with aqueous-methanolic silver nitrate led to an oxidative ring opening to give 2-methyl-1,4-diphenyl-4-benzoylcyclopent-1-ene (**24**). Analogy with observations of Padwa[6] suggested oxidative disengagement of a quaternary carbon in a tricyclo-[2.2.0.0^{2,6}]hexane. This is formulated in eq 2.



(2)

The reaction is parallel to the rhodium(I) oxidation of such tricyclics described by Katz.[7] Not only was the structure assigned to oxidation product **24** in conformity

(6) Padwa, A.; Blacklock, T. J.; Loza, R. *Tetrahedron Lett.* **1979**, 1671–1674.
(7) Roth, R. J.; Katz, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 4770–4771.

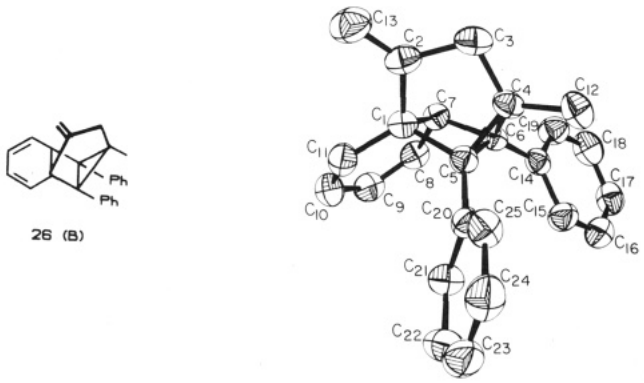
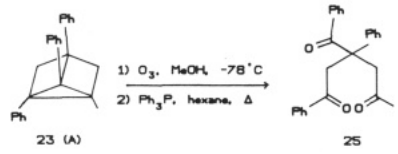


Figure 1. ORTEP drawing of 2-methylene-4-methyl-5,6-diphenyltetracyclo[5.4.0.0^{1,5}.0^{4,6}]undeca-8,10-diene.

with its spectral characteristics (note the Experimental Section) but also ozonolysis led to 1,3-diphenyl-3-benzoyl-1,5-hexanedione (**25**). The structure of this compound was assigned by its elemental analysis, the infrared spectrum revealing benzoyl and aliphatic carbonyls, the ^{1}H NMR indicating an unsplit methyl and two CH_2's, and the ^{13}C spectrum showing three carbonyl carbons and four aliphatic carbons.

Ozonolysis of photoproduct A followed by triphenylphosphine reflux in hexane led photoproduct A directly to trione **25**. Note eq 3. This reaction is unique in opening



(3)

all of the three-ring bonds. Although a single, pure ozonide was not isolated, it appeared that the role of the triphenylphosphine was conversion of ozonide isomers to trione **25**.

Thus, the formation of photoproduct A is as depicted in eq 9.

The structure of photoproduct B was pursued by spectral means (note Experimental Section); this indicated a complex structure containing a cyclohexadiene moiety. X-ray analysis led to structure **26**. An ORTEP drawing is shown in Figure 1.[8]

The formation of B is included in eq 9.

Turning attention to photoproduct C, we were led by the spectral data (note the Experimental Section) to employ ozonolysis which was found to afford a diketone with benzoyl and acetyl groups. Also, two CH_2's were noted and one of these seemed likely, by virtue of its coupling constant (J = 4 Hz), to be in a three ring. Hence structure **27** was entertained. Mild treatment of this diketone (i.e., **27**) led, in an interesting reverse Michael reaction, to the enedione **28** as outlined in Scheme III. The reaction was effected most readily with silica gel and likely results from unzipping of the monoenol **29**. The enedione **28**, in turn, was synthesized as outlined in Scheme III.

As a further check, the diketone ozonolysis product **27** was synthesized independently and proved identical with ozonolysis product before reverse Michael reaction. These details are included in Scheme III.

Finally, photoproduct C (i.e., **7**) itself was synthesized as noted above in Scheme I.

The formation of C is also included in eq 9.

Photoproduct D remained. This material proved identical with the 2-methyl-1,3-diphenyl-3-(2-phenylallyl)-

(8) Full X-ray details to be published by K. J. Haller and R. A. Bunce.

Scheme III. Synthesis of Degradation Products of Photoproduct C

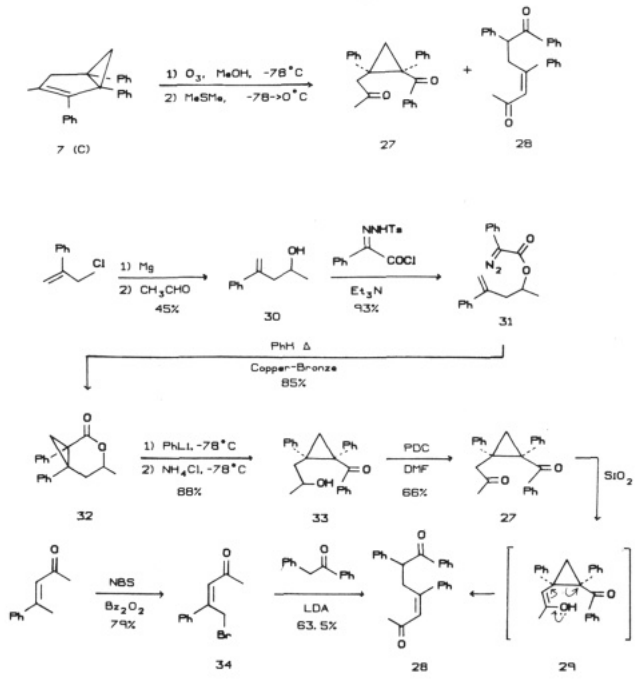


Table I. Comparison of NMR Spectral Data of Photoproducts B and E (Values in δ)

product	CH_2	CH_3	$=CH_2$	CH
B	2.97 (AB q)	0.95 (s)	4.57 (s) 4.67 (s)	3.02 (d)
E	2.94 (AB q)	0.90 (s)	4.68 (s) 4.75 (s)	3.00 (d)

cyclopropene (**2**) obtained in the original synthesis of photoreactant **1**. Note Scheme I again.

With all four photoproduct structures now known, the direct irradiation results can be summarized as in eq 9.

In continuing our exploratory photochemistry, we proceeded to *p*-(dimethylamino)benzophenone sensitization of 3-methyl-3-(phenylallyl)cyclopropene **1**. This led much more selectively to just photoproducts A and B. This, too, is outlined in eq 9.

Next we turned to the photochemistry of 2-methyl-1,3-diphenyl-3-(2-phenylallyl)cyclopropene (**2**) since this promised to shed some light on the mechanisms of the photochemistry of the 3-methyl-3-(phenylallyl)cyclopropene **1**. The direct photolysis was not investigated because of the complexity of the product distribution as a consequence of considerable light absorption by primary products relative to reactant **2**. In contrast, the sensitized irradiation afforded just two products in a ca. 10:1 ratio. The major photoproduct proved to be photoproduct A from irradiation of the 3-methyl-3-(phenylallyl)cyclopropene **1**.

The second photoproduct (E) observed had an NMR spectrum which was almost identical with that of photoproduct B in the irradiation of 3-methyl-3-(phenylallyl)-cyclopropene **1**. A comparison is given in Table I. Similarly, the ultraviolet spectra of photoproducts B and E were almost identical with a maxima at 222 nm (ϵ 33 460), 266 (5682), and 278 (5050). Intriguingly, the longer than normal wavelength absorption of these products seems possibly due to two σ bonds extending the cyclohexadiene π system to afford a benzenoid cycle.

With this data is was possible to formulate the structure of photoproduct E as 2-methylene-6-methyl-4,5-di-

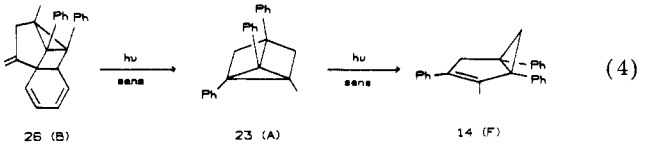
phenyltetracyclo[5.4.0.0^{1,5}.0^{4,6}]undeca-8,10-diene (**35**).

Hence, the triplet photochemistry of the 2-methyl-3-(phenylallyl)cyclopropene **2** can be formulated as in eq 10.

Further Photochemistry and Control Runs. Behavior of the Photoproducts. Photoproducts A, C, and D were found to be unreactive on direct irradiation. The sensitized photochemistry of photoproduct D has been discussed above. Photoproduct C was unreactive on sensitization.

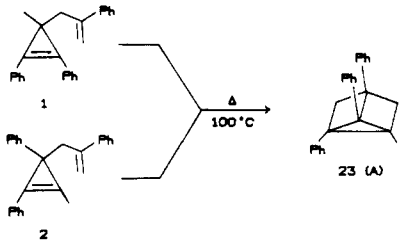
More interestingly, tetracyclic photoproduct B did react on direct irradiation and afforded the 3-methyl-3-(phenylallyl)cyclopropene **1**. This is included in eq 9. However, the relatively low reactivity signified that this reversion was not affecting the product distribution appreciably in the direct photolysis of 3-methyl-3-(phenylallyl)cyclopropene **1**.

Also, on sensitization, tetracyclic photoproduct B was slowly converted to tricyclic photoproduct A which, in turn, was very slowly converted to bicyclic photoproduct F. However, again, this conversion was inefficient enough that the primary cyclopropene photochemistry discussed above is not perturbed from that described. This is shown in eq 4. The structural assignment of photoproduct F (i.e., **14**) was based on the synthesis described above in Scheme I.



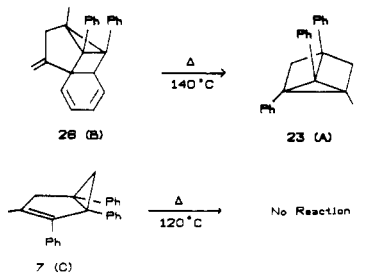
(4)

Thermal Chemistry of the Cyclopropenes and Some of Their Photoproducts. For comparative and mechanistic reasons the thermal chemistry of the cyclopropenes was investigated. Both 3-methyl-3-(phenylallyl)cyclopropene **1** and 2-methyl-3-(phenylallyl)cyclopropene **2** were found to rearrange at 100 °C to afford a single product which proved to be photoproduct A, that is, the tricyclo[2.2.0.0]hexane. This is depicted in eq 5.



(5)

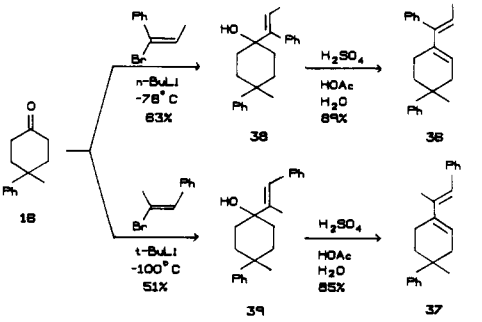
In further thermolyses, photoproducts B (i.e., the tetracyclic diene **26**) and C (i.e., the bicyclo[3.1.0]hexene **7**) were studied. The latter was stable at 120 °C, while at 140 °C the tetracyclic diene **26** led to the tricyclo[2.2.0.0]hexane (**23**), photoproduct A, as the stable product of these thermolyses. This is shown in eq 6.



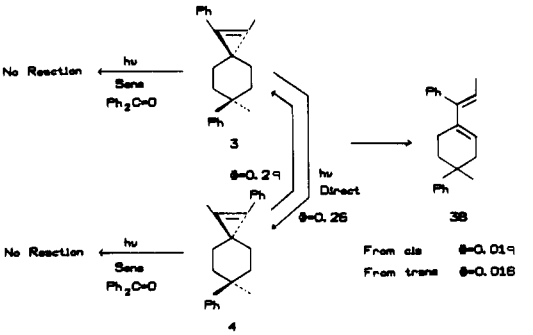
(6)

Photochemistry of the Cis and Trans Spirocyclopropenes. On direct irradiation both stereoisomers **3** and **4** were observed to interconvert with facility. A steady state comprising roughly equal amounts of the two resulted

Scheme IV. Syntheses of the Styrylcyclohexenes 36 and 37



Scheme V. Photochemistry of the Spirocyclopropenes

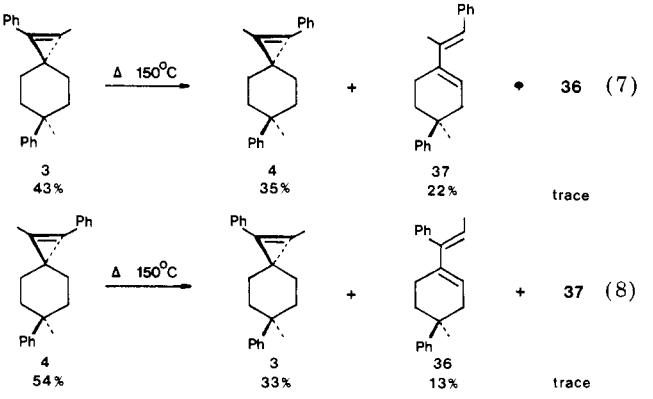


(vide infra for quantum yield data). In addition, a slow conversion of the cyclopropenes to a photoisomer was observed. This photoproduct proved to be 4-methyl-1-(*cis*-2-methyl-1-phenylethenyl)-4-phenyl-1-cyclohexene (**36**). This structure was established by independent synthesis as depicted in Scheme IV, which also includes the synthesis of the β-styrylcyclohexene **37** which was an a priori product and, indeed, was encountered in our research (vide infra).

In contrast, sensitization with benzophenone led to no reaction at all. This is discussed below. The course of the photochemistry, along with quantum yield results, is outlined in Scheme V.

Thermal Behavior of the Spirocyclopropenes. For comparison purposes and because of general interest the thermal behavior of the spirocyclopropenes was pursued. Indeed, the two stereoisomers equilibrated thermally at 150 °C.

What proved more dramatic was the conversion of each of the isomers to a different styrylcyclohexene. Thus, thermolysis of cis stereoisomer **3** of the spirocyclopropene afforded β-styrylcyclohexene **37**, while thermolysis of the trans spirocyclopropene **4** led to the previously encountered α-styrylcyclohexene **36**. Hence a regiospecific reaction[9] was occurring. This is shown in eq 7 and 8.

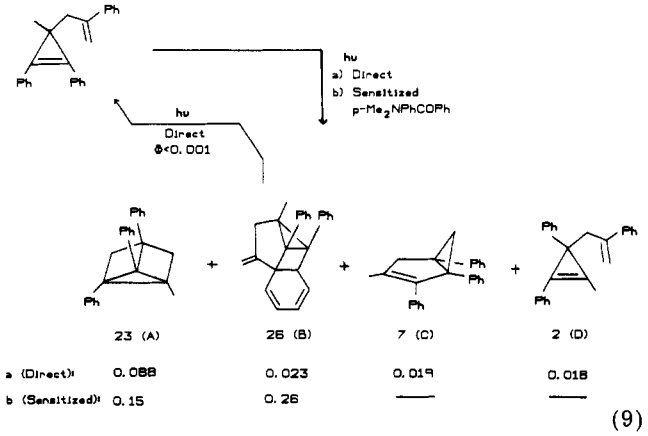


(7)

(8)

Quantum Yield Information. In order to cast more light on the reactivity and mechanisms of the photochemical reactions described above, we obtained both direct and sensitized quantum yields for the various transformations. All quantum yields given are values extrapolated to zero conversion.

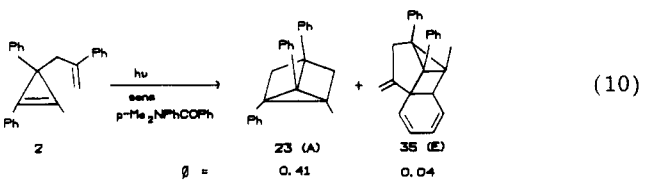
The direct quantum yields for the photochemical rearrangements of the 3-methyl-3-(phenylallyl)cyclopropene (1) are given, along with reaction products, in eq 9. It is



(9)

seen that the direct and sensitized product distributions are quite different, a point which is discussed in detail below. For the moment, however, we do note that while the sensitized product distribution does represent the behavior of the triplet reactant, the direct irradiation product distribution cannot be so simply interpreted.

Similarly, the quantum yield data on the triplet photochemistry of the 2-methyl-3-(phenylallyl)cyclopropene 2 are listed in eq 10.



(10)

Interpretative Discussion

Overall Reaction Course of the (Phenylallyl)cyclopropene Photochemistry. First we note that in the present study the behavior of the (phenylallyl)cyclopropene 1 contrasts with most of the allylcyclopropene photochemistry previously encountered.[4c,5] Thus, formation of tricyclo[2.2.0.0]hexanes as photoproduct A (i.e., **23**) has never been observed in the direct irradiations of allylcyclopropenes. Secondly, [2 + 2] cycloaddition of the cyclopropene π bond to the side-chain phenyl moiety to afford photoproduct B (i.e., **26**) is also without precedent. The more minor photoproducts, C (i.e., **7**) and D (i.e., **2**), however, have analogy.[4c,5]

In the case of the sensitized irradiations, the formation of the major photoproduct B (i.e., **26**) is, again, without precedent, while formation of the minor photoproduct A (i.e., **23**) is not unexpected.[4c,5]

Reaction Multiplicity. Although the molecular reaction mechanisms have not yet been considered, an orderly discussion is facilitated by first considering reaction multiplicities.

Two conclusions are easily made. Thus photoproducts C and D derive only from the singlet excited state, since these are not sensitized photoproducts (i.e., where the triplet is independently generated).

In the case of photoproducts A and B, it is clear from the sensitized runs (note eq 9) that these can derive from the triplet T_1. What we do not know, a priori, is whether in direct irradiations these two products come from rearrangements of the singlet S_1 or, instead, from T_1 after intersystem crossing from initially formed S_1.

Equations 11a and 11b are of help. These equations

$$\phi_A^{dir} = {}^1\phi_A + \phi_{isc}{}^3\phi_A \quad (11a)$$

$$\phi_B^{dir} = {}^1\phi_B + \phi_{isc}{}^3\phi_B \quad (11b)$$

are readily derived with the realization that quantum yields are really probabilities. Thus the quantum yield of formation of each of the photoproducts from direct irradiation is the sum of two probabilities: (i) that of reaction of the initially formed S_1 and (ii) the probability of intersystem crossing to the triplet multiplied by the probability of the triplet reacting once formed. Rearranging these two equations affords:

$${}^1\phi_A = \phi_A^{dir} - \phi_{isc}{}^3\phi_A \quad (12a)$$

$${}^1\phi_B = \phi_B^{dir} - \phi_{isc}{}^3\phi_B \quad (12b)$$

We wish to determine ${}^1\phi_A$ and ${}^1\phi_B$. Everything on the right of the equal signs is known except for ϕ_{isc}. Substitution of the values (eq 9) of the direct and sensitized quantum yields into eq 12a and 12b gives eq 13a and 13b. Here we take ${}^3\phi = \phi^{sens}$ with efficient energy transfer.

$$\phi_{isc} = (0.088 - {}^1\phi_A)/0.146 \quad (13a)$$

$$\phi_{isc} = (0.023 - {}^1\phi_B)/0.259 \quad (13b)$$

These equations allow us to set two limits. The first is on the intersystem crossing efficiency and the second is on the singlet quantum efficiencies ${}^1\phi_A$ and ${}^1\phi_B$.

Equation 13b sets the more stringent limits. Thus (note eq 13b) if the singlet quantum yield of formation of photoproduct B accounts for all of the direct irradiation efficiency (i.e., ${}^1\phi_B = 0.023$), then ϕ_{isc} is zero. If, instead, none of photoproduct B comes from the singlet (i.e., ${}^1\phi_B = 0$), then ϕ_{isc} is given by eq 13b as 0.089. This is the upper limit of the intersystem crossing efficiency in irradiation of the 3-methyl-3-(phenylallyl)cyclopropene 1. Use of eq 13a leads to a much less stringent upper limit.

If we now substitute this limiting value for ϕ_{isc} into eq 12a, we obtain a lower limit of 0.075 for ${}^1\phi_A$. The upper limit is 0.088, the direct quantum yield for formation of photoproduct A.

We conclude that most, if not all, of photoproduct A in the direct irradiation derives from S_1. This contrasts with the situation for photoproduct B where the evidence permits all or none, or intermediate amounts, to derive from S_1.

The preceding treatment is more generally and usefully stated. Thus in any case where two products are formed in different ratios in direct and sensitized irradiations, we may derive general limits on the amount of intersystem crossing and on the amount of photoproduct formed via S_1 in the direct irradiation. Proceeding along the same lines as the above, however, algebraically, we obtain

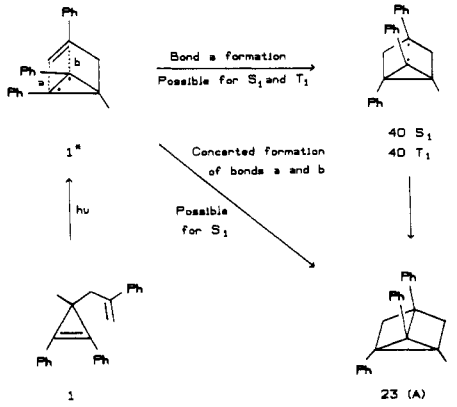
$$0 \le \phi_{isc} \le (\phi_B^{dir})/({}^3\phi_B) \quad (14a)$$

$$\phi_A^{dir} - ({}^3\phi_A)(\phi^{dir}{}_B)/({}^3\phi_B) \le {}^1\phi_A \le \phi_A^{dir} \quad (14b)$$

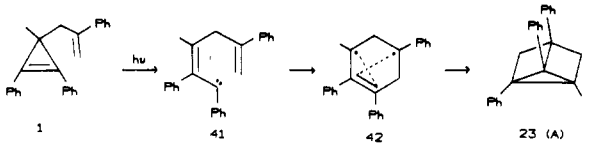
In selecting which of the two products is to be A and which is B, we pick B to be the product for which eq 14a gives the more stringent upper limit for ϕ_{isc}.

These relationships have proven useful in our research and we have termed these the "ratio bracketing rules" to distinguish them from the bracketing rule we described in one of our recent publications.[2a]

Scheme VI. Mechanism of Formation of Photoproduct A



Scheme VII. Alternative Singlet Mechanism for Formation of Photoproduct A



Formation of the Photoproducts. Photoproduct A. Of particular interest is the observation that the efficiency of formation of photoproduct A from S_1 falls in the range 0.075–0.088, that is, between 85% and 100% of the total for this compound. There is no precedent for formation of such tricyclo[2.2.0.0]hexanes from S_1, while abundant precedent[6,10] exists for formation from T_1. Two closely related mechanisms are shown in Scheme VI. An alternative possibility is shown in Scheme VII.

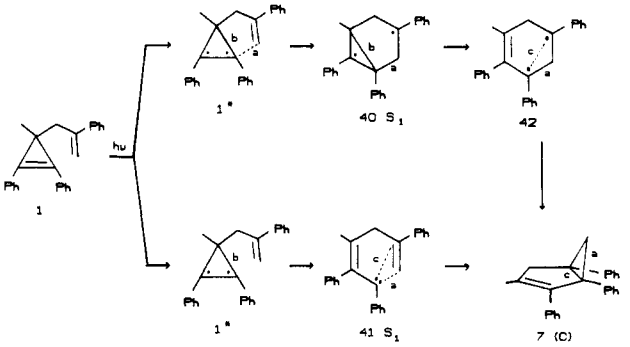
Scheme VI shows triplet biradical **40T_1** as the initial result of vinyl–vinyl bonding in the sensitized runs. For the singlet the corresponding singlet biradical **40S_1** can be written. However, for S_1 this version is just a gradation of the concerted [2 + 2] cycloaddition shown.

Scheme VII depicts an alternative mechanistic possibility. Since this mechanism begins with cyclopropene opening, a process not encountered for triplets,[2b,3] the mechanism is of value only for the singlet case. Here, a closure, possibly stepwise, of the carbene **41** leads to allylic biradical **42**, which then closes by 1,3-bridging of the allylic radical moiety and concomitant bonding of the central carbon of this moiety with the single, benzylic odd-electron center. While attack of an odd-electron moiety on the central carbon of an allylic radical species is unusual, it is not without precedent.[11] Such closures seem most favored where the central allylic carbon does not need to build up odd-electron density but bonds concertedly with an odd-electron center elsewhere. A weakness in this mechanism is that one of the three-ring bonds is broken in formation of the carbene, only to be reformed in the subsequent unorthodox double cyclization.

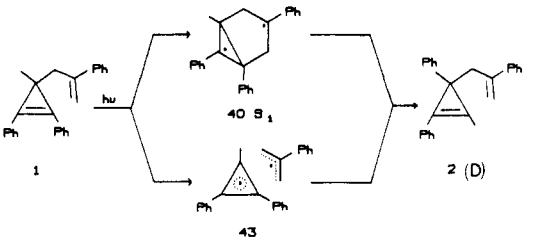
We note that at most 15% of photoproduct A can derive from intersystem crossing (vide supra) and that therefore if the mechanism in Scheme VI is correct, most of this reaction derives from an unprecedented S_1 cyclopropene [2 + 2] electrocyclic closure.

Formation of Photoproduct B. The cycloaddition involving the side-chain phenyl group is also without precedent. Yet the reaction is parallel to the [2 + 2] cycloaddition to the side-chain double bond. In both instances it seems that the cyclopropene moiety is unique in having a π system which cannot relax by twisting after electronic excitation. This feature may account for much of the varied and high reactivity of cyclopropene derivatives.

Scheme VIII. Mechanisms for Formation of Photoproduct C



Scheme IX. Mechanisms of Formation of Photoproduct D



Thus, the potential energy minimum for both S_1 and T_1 states of most alkenes has the two vicinal p orbitals perpendicular to one another,[12,13] while in cyclopropenes the energy minimum has the two p orbitals parallel. In such a species one has a particularly reactive moiety whose photochemistry has not been hitherto correlated to such a geometric and electronic constraint.[14]

Mechanism of Formation of Photoproduct C. Here two mechanisms are reasonable. The diradical bridging mechanism in Scheme VIII begins in parallel to the mechanism leading to photoproduct A as outlined in Scheme VI. Here vinyl–vinyl bridging leads to diradical 40S_1 (note both Schemes VI and VIII). This mechanism corresponds to that which we proposed[2b,3] for the rearrangements of vinylcyclopropenes to cyclopentadienes. In addition, this mechanism has been considered by Padwa and co-workers.[4b]

The second mechanism involves cyclopropene opening to afford the vinyldiradical (i.e., S_1 of the carbene) **41S_1**. This, too, is shown in Scheme VIII. We note that the carbene mechanism differs from the diradical pathway only in the chronology of bond breaking and formation. Thus in the diradical mechanism above, bond a is formed first, followed by scission of bond b. The reverse obtains for the carbene mechanism where bond b is broken first, followed by formation of bond a. The possibility of intermediate gradations between these two extremes has been noted in

(9) (a) Zimmerman, H. E.; Pasteris, R. J. *J. Org. Chem.* **1980**, *45*, 4864–4876. (b) *Ibid.* **1980**, *45*, 4876–4891. (c) See also ref 23.

(10) Padwa, A.; Blacklock, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 3390–3392.

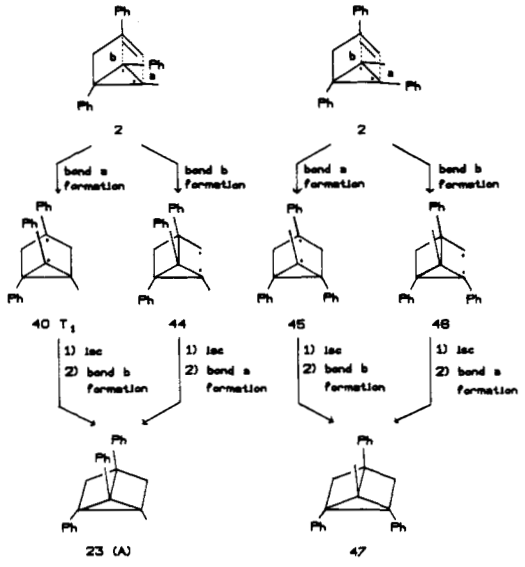
(11) Zimmerman, H. E.; Pincock, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 6208–6209.

(12) (a) Mulliken, R. S.; Roothaan, C. C. J. *Chem. Rev.* **1947**, *41*, 219–231. (b) Kaldor, U.; Shavitt, I. *J. Chem. Phys.* **1968**, *48*, 191–203.

(13) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1975**, *97*, 3718–3725.

(14) (a) An interesting example is the report[14b] that the 3-methyl-3-(2-phenylethyl)-1,2-diphenylcyclopropene triplet is unreactive. This is surprising since the skeleton closely resembles that of the 3-methyl-3-(phenylallyl)cyclopropene 1. (b) Padwa, A.; Chou, C. S.; Rosenthal, R. J.; Rubin, B. *J. Am. Chem. Soc.* **1981**, *103*, 3057–3068.

Scheme X. Two Possible Regioisomeric [2 + 2] Cycloaddition Modes for the 2-Methylcyclopropene



our earlier work[2b,3] and are likely. These mechanisms are considered further in connection with the photochemistry of the 2-methyl-3-(phenylallyl)cyclopropene **2**.

Mechanism of Formation of Photoproduct D. Formally, the conversion of the 3-methyl-3-(phenylallyl)-cyclopropene **1** to photoproduct D (i.e., **2**) is a photochemical Cope rearrangement. A reasonable mechanism, outlined in Scheme IX, involves initial vinyl–vinyl bonding to give the same diradical $40S_1$ postulated as leading to photoproducts A and C (note Schemes VI and VIII).

An alternative mechanism has been suggested by Padwa and co-workers[5b,15] for systems involving very stable diradicals. Applied to the present system, this affords a radical pair (**43**) which recombines. This process is suggested by scrambling of the ends of the allylic moiety in unsymmetrical examples.[5b,15] In these studies as well as the present one no cross-combination products were encountered. It is uncertain whether the radical–radical fission is a side process or the main reaction mechanism.

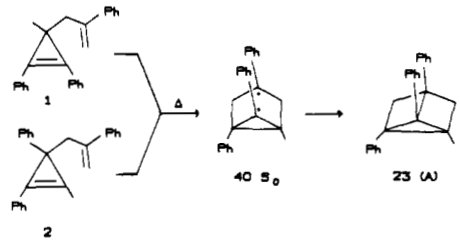
Mechanisms Involved in the Photochemistry of 2-Methyl-1,3-diphenyl-3-(2-phenylallyl)cyclopropene (2). For this compound the triplet behavior requires discussion. The major triplet product was photoproduct A (i.e., **23**, the tricyclo[2.2.0.0]hexane) formed in the photochemistry of the 3-methyl-3-(phenylallyl)cyclopropene **1**. This is of particular mechanistic interest, since a priori one might have anticipated formation of either photoproduct A or its regioisomer **47** from [2 + 2] cycloaddition. This is shown in Scheme X.

The marked regioselectivity leading to photoproduct A seems most likely to derive from the enhanced selectivity of a triplet diradical intermediate $40T_1$ which has both odd electrons delocalized by phenyl substituents. This diradical then undergoes intersystem crossing with formation of the second σ bond. The mechanisms leading to regioisomer **47** involve less delocalized diradicals, with only one phenyl group aiding in delocalization.

The minor photoproducts, E (i.e., tetracyclic **35**), must arise from a process quite similar to that encountered in the photochemistry of the 3-methylcyclopropene **1** whose mechanism has already been discussed in detail.

Special Cyclopropene Reactivity Deriving from Lack of Flexibility. One item of particular interest is

Scheme XI. Mechanism of the Thermal Rearrangements of the 2-Methyl- and 3-Methyl-3-(phenylallyl)cyclopropenes



the unusual reactivity and diverse modes of behavior of cyclopropene excited states, both singlet and triplet. Thus, cyclopropenes have been observed to: (a) vinyl–vinyl bridge,[2b,3-5] (b) hydrogen abstract,[14b,16] (c) cycloadd to aromatic rings as in the present study, and (d) open to afford carbenes.[2b,3-5]

All of this is behavior not common in ordinary alkene photochemistry. It seems likely that cyclopropenes are anomalous because the excited states are, of necessity, planar in contrast to ordinary alkenes[12,13] where the excited state singlet or triplet relaxes to a perpendicular species to the extent permitted by molecular geometry. The twisted excited states become close to degenerate with the ground state very quickly along the reaction hypersurface, thus allowing radiationless decay and inhibiting reaction. Therefore, in simple alkenes one never can observe reactivity characteristic of a planar $\pi-\pi$ excited state. Conversely, cyclopropene excited states remain nondegenerate with S_0 reasonably far along the reaction hypersurface.

Thermal Chemistry of the (Phenylallyl)cyclopropenes. The formation of the tricyclic [2.2.0.0]hexane **23** (i.e., photoproduct A) from the 100 °C thermolysis of both the 3-methyl- and the 2-methyl-3-(phenylallyl)-cyclopropenes **1** and **2** is of interest. This intriguing demonstration of the high strain energy of the cyclopropene (54 kcal/mol[17]) is a reaction previously reported by Padwa and co-workers.[10,18] A contrast is seen in the low temperature required for the presently studied systems compared to those by Padwa where the rearrangements proceeded only at 150–170 °C. One difference is the extra delocalization afforded by the phenyl group on the allyl moiety when one considers the reaction mechanism (note Scheme XI) as proposed by Padwa.[10,18]

We note that the same diradical $40S_0$ is formed from the two cyclopropene reactants in accord with observation of the same product in the two cases. While any 2-methylcyclopropene **2** formed in the thermolysis of the 3-methyl isomer **1** would react further very rapidly (vide supra) and thus not be observed, the thermolysis of the 2-methylcyclopropene **2** to afford the 3-methyl isomer would be expected to afford discernible amounts of any 3-methyl isomer **1** formed, since the conversion of isomer **1** to tricyclic product **23** is slow enough for detection.

We also note that counterpart diradicals, $40S_1$ (note Schemes VIII and IX) and $40T_1$ (note Scheme X) have already been considered in connection with the photochemistry discussed above. Thus, $40S_1$ was proposed as being an intermediate in conversion of the 3-methyl-3-(phenylallyl)cyclopropene **1** to afford photoproduct D (i.e.,

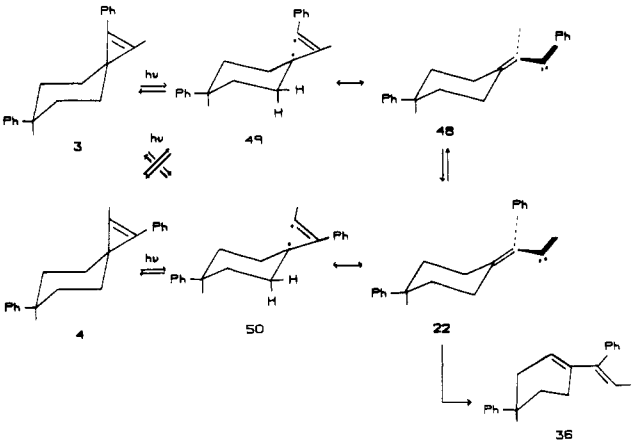
(15) Padwa, A.; Blacklock, T. J.; Loza, R. *Tetrahedron Lett.* **1979**, 219–222.

(16) Padwa, A.; Blacklock, T. J.; Chou, C. S.; Hatanaka, N. *J. Am. Chem. Soc.* **1979**, *101*, 5743–5757.

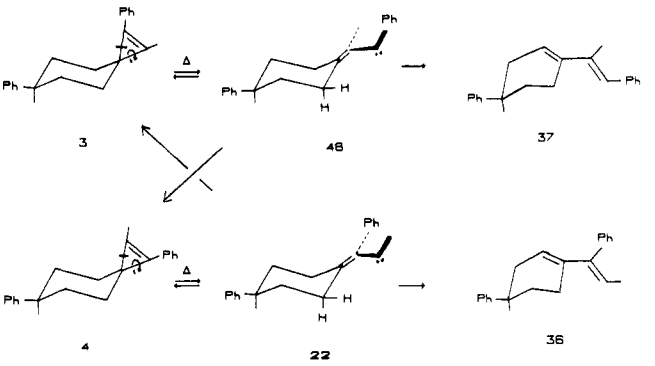
(17) Schleyer, P. v. R.; Williams, J. E., Jr.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377–2386.

(18) (a) Padwa, A.; Blacklock, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 1321–1323. (b) *Ibid.* **1980**, *102*, 2797–2806.

Scheme XII. Mechanisms for the Photochemical Reactions of the Spirocyclopropenes



Scheme XIII. Thermal Mechanism of Spirocyclopropene Reaction



2) and as a likely intermediate leading to photoproducts A (i.e., **23**) and C (**7**). Similarly, **40T$_1$** was advanced as leading from the triplet of the 2-methyl-3-(phenylallyl)-cyclopropene **2** to the tricyclic [2.2.0.0]hexane **23** (photoproduct A).

However, since thermal generation of diradical **40**, direct irradiation formation of **40**, and the sensitized approach to **40** all afford different products, we must conclude that several different electronic states (i.e., S_0, S_1, and T_1) are responsible for the different behaviors. The difference in behaviors is not an artifact, since in each case the products not encountered are stable to reaction conditions as established in control runs (vide supra).

Evidence for the role of different diradical excited states in affording different product distributions has precedent in our earlier investigations.[19-23] The one exception to this difference is the formation of tricyclo[2.2.0.0]hexane **23** (photoproduct A) from both thermolysis and sensitized irradiation, that is, from S_0 and T_1.

Reactivity of the Allylcyclopropenes Despite the Presence of a Potential Free Rotor. With a terminal vinyl moiety one might have anticipated low reactivity due to the free rotor effect,[24,25] especially in the case of the triplet. However, we note that the low-energy chromophore in **1** but not **2** is the ring, *cis*-stibenyl group and that the PhC(=CH$_2$) free rotor is of higher energy. In such instances, one expects an inhibited decay of the free-rotor type. Additionally, as noted earlier,[25] very rapid rearrangements may merely compete more effectively than free-rotor decay.

Mechanisms in the Chemistry of the Spirocyclopropenes. Scheme V outlines the photochemical behavior of the spirocyclopropenes and eq 7 and 8 describe the thermal behavior. All of these reactions can be most reasonably ascribed to carbene intermediates. Throughout, the preferred behavior of the ring-opened carbenes is reclosure to give the spirocyclopropene stereoisomers. This may simply derive from the low activation energy required for closure of two valence deficient centers. The slower formation of dienes **36** and **37** requires hydrogen transfer. Mechanisms for the interconversions and hydrogen transfer in the photochemistry are shown in Scheme XII.

One interesting point is that both stereoisomers of the spirocyclopropenes **3** and **4** lead to the same regioisomer of diene product (i.e., to **36**), that is, lack of regiospecificity[9] in the face of regioselectivity.

The preference for opening of the bond with methyl substitution must derive from a complex steady-state situation as depicted in Scheme XII.

If one makes use of the observation from the thermal experiments that the S_0 carbene is capable of the γ-hydrogen abstraction, it seems plausible that the carbenoid species (i.e., a vinyl diradical **49** and **50**) initially formed in the photolyses must first internally convert to S_0 before hydrogen abstracting. It is equally plausible that the initially opened species can reclose to spirocyclopropene. Then, it is possible that it is the rate of internal conversion to S_0 carbene which dominates and determines which bond-opened species proceeds onward in the photochemical rearrangement to afford diene **36**.

It may be that one carbene (i.e., **22**) is sufficiently more available or reactive that only it is seen reflected in the photochemistry. This could be a result of more rapid decay from a S_1 carbene to S_0 where the carbenoid carbon is methyl substituted rather than phenyl bearing.

In the thermolysis (note Scheme XIII) rather novel regiospecificity[9] is encountered wherein each spiro stereoisomer gives rise to a different diene. Thus, cis spiro isomer **3** led to diene **37** in which the phenyl-bearing carbon had been cleaved while trans spiro isomer **4** led to diene **37** in which the methyl-bearing carbon had been severed. While this rearrangement of cyclopropenes to afford dienes has precedent,[26] the regiospecificity does not.

The mechanism may be considered from an MO vantage point. Thus, MO following[27] permits us to formulate the MO transformation for reactions lacking symmetry. This reasoning is applied to the cyclopropene opening to afford

(19) Thus, the penultimate intermediate in the barrelene to semibullvalene di-π-methane rearrangement was a diradical; this diradical behaved differently depending on its state.[20] Another example was the differing behavior of the cyclopropyl dicarbinyl diradical encountered in the bicycle and reverse di-π-methane rearrangements.[21-23] Here the ground-state diradical underwent a central σ-bond fission with reverse di-π-methane behavior, while the S_1 state led to bicycling.

(20) Zimmerman, H. E.; Boettcher, R. J.; Buehler, N. E.; Keck, G. E.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 7680–7689.

(21) Zimmerman, H. E.; Armesto, D.; Amezua, M. G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367–6383.

(22) Zimmerman, H. E.; Factor, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 3538–3548.

(23) Zimmerman, H. E.; Factor, R. E. *Tetrahedron* **1981**, *37*, 125–141.

(24) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1972**, *96*, 8749–8761.

(25) (a) Zimmerman H. E. In "Rearrangements in Ground and Excited States", DeMayo, P. Ed.; Academic Press: New York, 1980; Vol. 3, Chapter 16, pp 13–166. (b) Zimmerman, H. E.; Samuelson, G. E. *J. Am. Chem. Soc.* **1969**, *91*, 5307–5318. (c) Zimmerman, H. E.; Albrecht, F. X.; Haire, M. J. *Ibid.* **1975**, *97*, 3726–3740. (d) Zimmerman, H. E.; Kurtz, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 8210–8212 (footnote 6). (e) Zimmerman, H. E.; Klun, R. T. *Tetrahedron* **1978**, *34*, 1775–1803. (f) References 3, 13, 21 (especially footnote 11), and 24.

(26) (a) Stechl, H. *Chem. Ber.* **1964**, *97*, 2681–2688. (b) Srinavasan, R. *Chem. Commun.* **1971**, 1041–1042. (c) York, E. J.; Dittmar, W.; Stevenson, J. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 2882–2883. (d) *Ibid.* **1973**, *95*, 5680–5687. (e) Streeper, R. D.; Gardiner, P. D. *Tetrahedron Lett.* **1973**, 767–770.

(27) Zimmerman, H. E. *Acc. Chem. Res.* **1972**, *5*, 393–401.

carbene **22** or **48** (Figure 2). Similarly, the subsequent hydrogen abstraction of a ring hydrogen by the carbenoid center to afford diene (i.e., **36** or **37**) also is treated.

An exciting point is noted. While each of the two reaction stages is separately thermally allowed, a concerted version, in which a discrete carbene intermediate reacts as it is formed, is forbidden. This can be seen at the carbene stage of the reaction where it is a different linear combination of the two p orbitals at the carbene center which requires s character for the two reaction stages.

While the regiospecificity may arise merely from greater relief of strain in opening the axial bond, the MO treatment suggests a more intriguing possibility. Twisting is required about the σ bond holding the cyclopropene double bond to the six-membered ring (note Figure 2). The cyclopropene double bond adjacent to the six ring bears a phenyl or methyl group and such twisting is severely sterically inhibited for a residual axial but not an equatorial σ bond.

Finally, the vinyl diradical in the photochemical reaction is seen not to require twisting in its formation. Thus, the inhibition of twisting of an equatorially opened cyclopropene is not involved.

Conclusion

The photochemistry of cyclopropenes can be seen to be especially rich in the varied types of photochemical reactions encountered. The subtle variation of reaction encountered with structural variation provides both a mechanistic challenge and a promise of reward.

Experimental Section[28]

***trans*-2-Methyl-1,3-diphenyl-2-propen-1-one Tosylhydrazone.** This material was prepared as described for the 3,4-diphenyl-3-buten-2-one[3b] in 72.1% yield, mp 165–166 °C. The spectral data were as follows: NMR ($CDCl_3$) τ 2.20 (d, J = 9.0 Hz, 2 H, arom), 2.44–3.08 (m, 12 H, arom), 3.76 (s, 1 H, vinyl), 7.60 (s, 3 H, CH_3), 7.65 (s, 3 H, CH_3); IR ($CHCl_3$) 3.09, 3.30, 3.33, 3.45, 3.55, 6.29, 6.76, 6.97, 7.33, 7.52, 8.64, 8.97, 9.22, 9.43, 9.80, 10.93, 11.36, 12.42, 14.49, 14.93, 15.38 μm; MS, m/e 390.1407 (calcd for $C_{23}H_{22}N_2O_2S$, m/e 390.1402).

Anal. Calcd for $C_{23}H_{22}N_2O_2S$: C, 70.75; H, 5.69. Found: C, 70.62; H, 5.76.

2-Methyl-1,3-diphenylcyclopropene. This material was prepared by an improved procedure,[28a] employing the above tosylhydrazone. Thus a more facile reaction was obtained by use of *tert*-butyl alcohol and sodium hydride in 9:1 pentane/diglyme. The product was converted to 3-methyl-1,2-diphenylcyclopropenyl fluoroborate.[3b]

3-Hydroxy-2-phenylpropene. Into a stirred 50 °C solution of (1-phenylethenyl)magnesium bromide,[31] prepared from 91.5 (0.50 mol) of 1-bromo-1-phenylethene[32] and 12.0 g (0.50 mol) of magnesium metal, was bubbled gaseous formaldehyde generated by 160 °C pyrolysis of paraformaldehyde. The reaction mixture was cooled and quenched slowly with 15 mL of saturated ammonium chloride and the precipitate was filtered and washed with ether and tetrahydrofuran. The filtrate was washed with water and saturated sodium chloride, dried over anhydrous magnesium sulfate, concentrated in vacuo, and distilled at 1.5 mm (ca. 100 mg of 2,6-di-*tert*-butyl-4-methylphenol was added as a stabilizer) to afford 44.0 g (0.33 mol, 63.5%) of pure 3-hydroxy-2-phenylpropene, bp 79–82 °C (lit.[33] bp 106–107 °C).

3-Chloro-2-phenylpropene. The following procedure is based on but modified from the general method of Collington and Meyers.[34] A stirred soluton of 35.0 g (0.26 mol) of 3-hydroxy-2-phenylpropene in 35.0 g (0.28 mol) of *s*-collidine was treated with a solution of 11.2 g (0.26 mol) of lithium chloride in a minimum of anhydrous dimethylformamide. When the mixture was cooled to 0 °C, a heavy suspension was formed. This was treated dropwise with 33.0 g (0.28 mol) of methanesulfonyl chloride, stirring was continued with gradual warming to 25 °C during 8 h, and the pale-yellow mixture was poured into ice water and extracted with 1:1 ether/pentane. The organic layer was washed several times with water and once with saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated at reduced pressure to provide 36.0 g (0.4 mol, 90.7%) of the crude allylic chloride. Vacuum distillation then afforded 34.8 g (0.23 mol, 87.8%) of pure 3-chloro-2-phenylpropene, bp 45–50 °C (0.7 mm) [lit.[33] bp 87–88 °C (5 mm)].

3-Methyl-1,2-diphenyl-3-(2-phenylallyl)cyclopropene and 2-Methyl-1,3-diphenyl-3-(2-phenylallyl)cyclopropene. The preparation of (2-phenylallyl)magnesium chloride was performed by use of a modification of the general procedure of Kinnel et al.[35] for this difficult case by reacting 10.0 g (65.8 mmol) of 3-chloro-2-phenylpropene under high dilution conditions in 125 mL of refluxing anhydrous tetrahydrofuran with 15.0 g (0.63 mol) of magnesium metal. The solution was cooled and transferred at room temperature to a stirred suspension of 4.00 g (13.7 mmol) of 3-methyl-1,2-diphenylcyclopropenyl fluoroborate in 25 mL of anhydrous tetrahydrofuran. The reaction mixture was stirred for 1.5 h and quenched with saturated ammonium chloride and was ether extracted. The combined extracts were washed with water and saturated sodium chloride and concentrated in vacuo. Purification was carried out, two runs at a time, by column chromatography on a 300 cm × 2.0 cm silica gel column eluted with hexane in 40-mL fractions with eluent monitored at 282 nm to give the following: 1–15, nil; 16–30, 0.17 g (1.44 mmol) of 2-phenylpropene; 31–70, 0.94 g (4.02 mmol) of 2,5-diphenyl-1,5-hexadiene; 71–80, nil; 81–215, 3.01 g (9.35 mmol, 34.1%) of 3-methyl-1,2-diphenyl-3-(2-phenylallyl)cyclopropene as a light-yellow oil; 216–289, nil; 290–535, 1.97 g (6.11 mmol, 22.3%) of 2-methyl-1,3-diphenyl-3-(2-phenylallyl)cyclopropene as a light-yellow oil.

(28) (a) Some experimental procedures have been truncated or deleted. In some cases, superior methods for synthesis of materials were developed. These are described in full in the Ph.D. Thesis of R. A. Bunce, University of Wisconsin, 1981. (28)(b) All melting points were determined by using a calibrated hot stage apparatus. Mass spectra were obtained with an AEI MS-902 mass spectrometer at 70 eV. Proton nuclear magnetic resonance spectra were obtained with a JEOL MH-100 spectrometer and both proton and carbon nuclear magnetic resonance spectra were obtained with a JEOL FX-200 spectrometer. Infrared spectra were obtained on either a Perkin-Elmer IR-267 or a Beckman Acculab 7 spectrophotometer and ultraviolet spectra were recorded with a Cary Model-15 or Model-118C spectrophotometer.

All reactions were run under an atmosphere of dry nitrogen unless otherwise specified. Column chromatography was performed on silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) or alumina (Fisher, 80–200 mesh) as specified, packing mixed with Sylvania 2282 phosphor and slurry packed into Vycor columns such that band elution could be monitored with a hand-held UV lamp. Preparative thick-layer chromatography was carried out with MN-Kieselgel G/UV 254 silica gel. High-pressure liquid chromatography (HPLC) was performed on a Waters ALC-100 liquid chromatograph with polished stainless steel columns of various lengths packed with 10–15-μm porous silica microbeads[29] eluents monitored by means of an LDC 254-mn UV detector calibrated for relative responses of detected compounds and standards. The pentane utilized in HPLC work was washed with 1:1 concentrated sulfuric acid/concentrated nitric acid, 5% aqueous acidic potassium permanganate, 10% aqueous potassium hydroxide, water, and saturated sodium chloride, dried over anhydrous magnesium sulfate, and distilled from lithium aluminum hydride under nitrogen atmosphere.

Benzene used in irradiation experiments was washed with concentrated sulfuric acid, 5% aqueous acidic potassium permanganate, 10% aqueous potassium hydroxide, water, and saturated sodium chloride, dried over anhydrous magnesium sulfate, and distilled from calcium hydride under a nitrogen atmosphere. Photolysis grade cyclohexane was prepared in an analogous manner except the initial acid wash was with 1:1 concentrated sulfuric/concentrated nitric acid. Nitrogen employed in photolyses was deoxygenated by percolation through sodium vanadate/zinc amalgam solution and dried before use. Glassware used in photochemical work was soaked with 0.01 N sodium hydroxide for 30 min and then rinsed with ethanol, ether, and benzene prior to each run.

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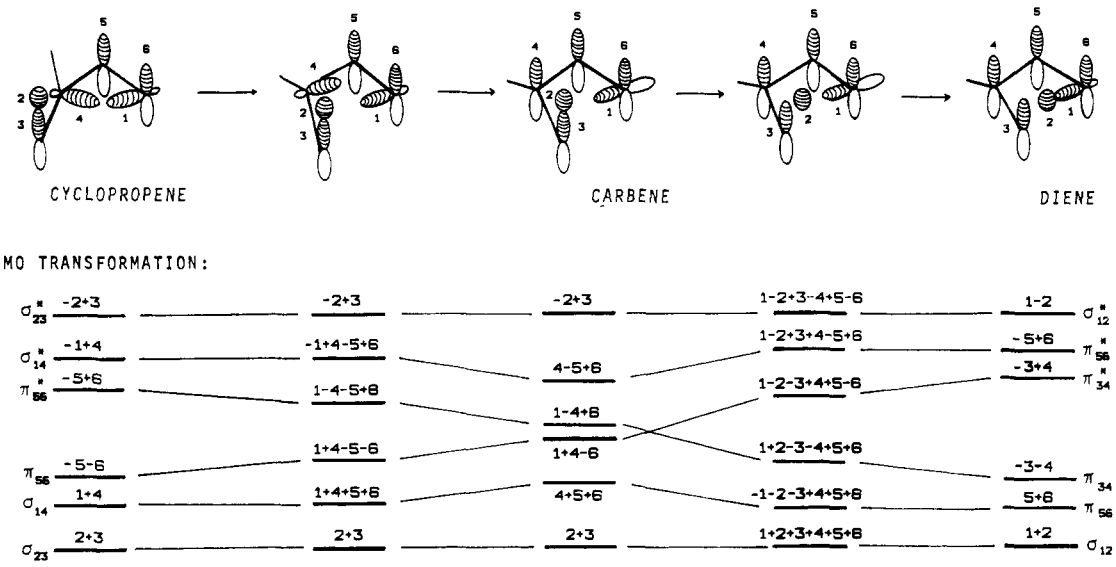

Figure 2.

The spectral data for 3-methyl-1,2-diphenyl-3-(2-phenylallyl)cyclopropene were as follows: NMR (CCl_4) τ 2.56–3.18 (m, 15 H, arom), 4.92 (s, 1 H, vinyl), 5.00 (s, 1 H, vinyl) 6.92 (s, 2 H, CH_2), 8.54 (s, 3 H, CH_3); ^{13}C NMR (C_6D_6) 148.4, 142.2, 130.6, 129.4, 128.5, 128.4, 128.1, 127.9, 127.4, 127.0, 123.2, 114.9, 45.6, 25.2, 23.1 ppm; IR (thin film) 3.25, 3.27, 3.28, 3.30, 3.38, 3.41, 3.43, 3.50, 5.53, 6.15, 6.26, 6.36, 6.70, 6.92, 7.30, 9.35, 9.78, 11.21, 12.92, 13.30, 14.39, 14.56 μm; UV (95% EtOH) 231 nm (ϵ 30956), 321 (26250); MS, m/e 322.1723 (calcd for $C_{25}H_{22}$, m/e 322.1721).

Anal. Calcd for $C_{25}H_{22}$: C, 93.16; H, 6.84. Found: C, 92.99; H, 7.16.

The spectra for 2-methyl-1,3-diphenyl-3-(2-phenylallyl)cyclopropene were as follows: NMR (CCl_4) τ 2.60–3.00 (m, 15 H, arom), 4.84 (s, 1 H, vinyl), 5.02 (s, 1 H, vinyl), 6.37 (d, A of AB q, J = 16.0 Hz, 1 H, CH), 6.84 (d, B of AB q, J = 16.0 Hz, 1 H, CH), 8.16 (s, 3 H, CH_3); CMR (C_6D_6) 148.0, 147.3, 142.6, 129.6, 129.0, 128.6, 128.5, 128.4, 128.0, 127.7, 127.5, 127.2, 126.8, 125.2, 116.3, 115.0, 41.3, 31.6, 9.3 ppm; IR (thin film) 3.25, 3.27, 3.30, 3.31, 3.38, 3.44, 3.50, 5.40, 5.97, 6.15, 6.26, 6.36, 6.69, 6.93, 7.33, 8.50, 8.67, 9.09, 9.34, 9.75, 9.98, 11.15, 12.85, 13.00, 13,19, 14.35 μm; UV (95% EtOH) 252 nm (ϵ 18579), 284 (10382); MS, m/e 322.1711 (calcd for $C_{25}H_{22}$, m/e 322.1721).

Anal. Calcd for $C_{25}H_{22}$: C, 93.16, H, 6.84. Found: C, 92.78; H, 7.15.

Exploratory Direct Photolysis of 3-Methyl-1,2-diphenyl-(2-phenylallyl)cyclopropene. High-Conversion Run and Product Isolation. A 750-mL benzene solution of 1.44 g (4.47 mmol) of 3-methyl-1,2-diphenyl-3-(2-phenylallyl)cyclopropene was photolyzed through filter A on the black box apparatus[36] for 4.75 h (2.15 mEinsteins, 56% conversion). Concentration under vacuum at 25 °C afforded 1.47 g of a yellow oil, which was applied to six 20 cm × 20 cm thick layer plates and eluted 8 times with hexane to give a separation of five distinct bands. Workup and spectroscopic analysis of the products gave the following: band 1, R_f 0.86, 0.17, g (0.53 mmol, 11.9%) of 2-methylene-4-methyl-5,6-diphenyltetracyclo[5.4.0.0^{1,5}.0^{4,6}]undeca-8,10-diene, mp 127–128 °C; band 2, R_f 0.76, 0.58 g (1.80 mmol, 40.3%) of unreacted 3-methyl-1,2-diphenyl-3-(2-phenylallyl)-cyclopropene; band 3, R_f 0.65, 0.28 g (0.87 mmol, 19.5%) of 2-methyl-1,4,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane as a light-yellow oil; band 4, R_f 0.61, 0.10 g (0.31 mmol, 6.9%) of 2-methyl-1,3-diphenyl-3-(2-phenylallyl)cyclopropene as a clear oil; band 5, R_f 0.46, 0.09 g (0.28 mmol, 6.3%) of 3-methyl-1,2,5-triphenylbicyclo[3.1.0]hex-2-ene, mp 108–109 °C.

The spectral data for 2-methylene-4-methyl-5,6-diphenyltetracyclo[5.4.0.0^{1,5}.0^{4,6}]undeca-8,10-diene were as follows: NMR ($CDCl_3$) τ 2.70–3.00 (m, 10 H, arom), 4.24 (m, 2 H, 2 vinyl), 4.50 (m, 1 H, vinyl), 4.96 (m, 1 H, vinyl), 5.33 (s, 1 H, vinyl), 5.43 (s, 1 H, vinyl), 6.79 (d, A of AB q, J = 17.0 Hz, 1 H, CH), 6.98 (d, J = 2.0 Hz, 1 H, CH), 7.28 (d, B of AB q, J = 17.0 Hz, 1 H, CH), 0.95 (s, 3 H, CH_3); ^{13}C NMR (acetone-d_6) 159.0, 147.0, 137.4, 134.4, 131.8, 129.8, 129.1, 128.5, 128.4, 127.3, 126.6, 125.5, 123.6, 122.0, 117.2, 56.1, 54.9, 47.1, 45.2, 38.4, 34.0, 15.5 ppm; IR ($CHCl_3$) 3.29, 3.32, 3.36, 3.45, 3.53, 6.06, 6.26, 6.71, 6.94, 7.26, 9.35, 9.71, 9.85, 11.39, 14.49 μm; UV (95% EtOH) 222 nm (ϵ 33462), 266 (5682), 278 (5050); MS, m/e 322.1714 (calcd for $C_{25}H_{22}$, m/e) 322.1721).

Anal. Calcd for $C_{25}H_{22}$: C, 93.16; H, 6.84. Found: C, 93.15; H, 6.67.

The spectral data for 2-methyl-1,4,6-triphenyltricyclo-[2.2.0.0^{2,6}]hexane were as follows: NMR (CCl_4) τ 2.64–3.16 (m, 15 H, arom), 6.88 (d, A of AB q, J = 8.0 Hz, 1 H, CH), 7.08 (d, A of AB q, 1 H, CH), 7.26 (d, B of AB q, J = 8.0 Hz, 1 H, CH), 7.52 (d, B of AB q, 1 H, CH), 8.58 (s, 3 H, CH_3); ^{13}C NMR (C_6D_6) 140.9, 139.2, 134.5, 128.9, 128.4, 128.2, 128.1, 127.9, 127.4, 127.0, 126.6, 126.2, 125.9, 62.9, 53.6, 46.2, 44.7, 40.7, 36.8, 12.5 ppm; IR (thin film) 3.24, 3.26, 3.28, 3.39, 3.48, 6.27, 6.71, 6.94, 7.26, 7.52, 8.33, 8.50, 8.70, 9.39, 9.76, 11.21, 12.85, 13.33, 14.02, 14.51 μm; UV (95% EtOH) 230 nm (ϵ 14702); MS m/e 322.1711 (calcd for $C_{25}H_{22}$, m/e 322.1711).

Anal. Calcd for $C_{25}H_{22}$: C, 93.16; H, 6.84. Found: C, 92.98; H, 6.95.

The spectral data for 3-methyl-1,2,5-triphenylbicyclo[3.1.0]-hex-2-ene were as follows: NMR (CCl_4) τ 2.67–3.20 (m, 15 H, arom), 6.70 (d, A of AB q, J = 18.0 Hz, 1 H, CH), 7.18 (d, B of AB q, J = 18.0 Hz, 1 H, CH), 7.66 (d, J = 4.0 Hz, 1 H, cyclopropyl), 8.08 (s, 3 H, CH_3), 8.83 (d, J = 4.0 Hz, 1 H, cyclopropyl); ^{13}C NMR (C_6D_6) 142.3, 141.8, 138.6, 137.2, 133.9, 129.4, 129.1, 129.0, 128.0, 127.7, 126.3, 126.0, 125.5, 51.0, 49.8, 37.6, 25.5, 15.1 ppm; IR (KBr) 3.25, 3.27, 3.29, 3.31, 3.35, 3.44, 3.47, 3.48, 3.55, 6.28, 6.71, 6.94, 7.95, 9.34, 9.80, 9.90, 12.67, 12.84, 13.32, 13.93, 14.49 μm; UV (95% EtOH) 223 nm (ϵ 19923), 254 (12689); MS m/e 322.1714 (calcd for $C_{25}H_{22}$, m/e 322.1721).

Anal. Calcd for $C_{25}H_{22}$: C, 93.16; H, 6.84. Found: C, 92.95; H, 7.02.

Exploratory Sensitized Photolysis of 3-Methyl-1,2-diphenyl-3-(2-phenylallyl)cyclopropene. High-Conversion Run and Product Isolation. A 750-mL benzene solution of 505 mg (1.57 mmol) of 3-methyl-1,2-diphenyl-3-(2-phenylallyl)cyclopropene and 4.00 g (17.8 mmol) of *p*-(dimethylamino)benzophenone was photolyzed through filter B on the black box apparatus[36] for 3.53 h (2.14 mEinsteins, 82.5% conversion). The solution was concentrated in vacuo without heat and *p*-(dimethylamino)benzophenone (3.99 g, 17.8 mmol, 100%) was recovered by filtering the concentrated photolysate through a silica gel pad with hexane. Concentration of the hexane filtrate then

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afforded 510 mg of a light-yellow oil, which was applied to three 20 × 20 cm thick layer plates. Elution 8 times with hexane gave three distinct bands: band 1, R_f 0.88, 0.27, g (0.84 mmol, 53.4%) of 2-methylene-4-methyl-5,6-diphenyltetracyclo[5.4.0.0^{1,5}.0^{4,6}]-undeca-8,10-diene, mp 127–128 °C; band 2, R_f 0.79, 0.09 g (0.28 mmol, 17.7%) of unreacted 3-methyl-1,2-diphenyl-3-(2-phenylallyl)cyclopropene; band 3, R_f 0.67, 0.11 g (0.34 mmol, 21.8%) of 2-methyl-1,4,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane. The spectral data were identical with those reported earlier.

Single-Crystal X-ray Structure of 2-Methylene-4-methyl-5,6-diphenyltetracyclo[5.4.0.0^{1,5}.0^{4,6}]undeca-8,10-diene. Full details of the X-ray crystal structure determination of 2-methylene-4-methyl-5,6-diphenyltetracyclo[5.4.0.0^{1,5}.0^{4,6}]undeca-8,10-diene are being published independently by Haller and Bunce.[8]

Bromine Treatment of 2-Methyl-1,4,6-triphenyltricyclo-[2.2.0.0^{2,6}]hexane. Elucidation of the Molecular Skeleton and Substitution Pattern. To a stirred 10 mL −78 °C methylene chloride solution of 468 mg (1.46 mmol) of 2-methyl-1,4,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane was added dropwise a solution of 233 mg 0.08 mL, 1.46 mmol) of bromine in 5 mL of methylene chloride. The solution decolorized instantly and was concentrated in vacuo at ambient temperature. The brown oil obtained was chromatographed on a 25 cm × 1.0 cm column of alumina. Elution with 250 mL of hexane afforded 273 mg (0.85 mmol, 58.3%) of 2,3,5-triphenyltoluene following recrystallization from methanol, mp 88–89 °C. The spectral properties were as follows: NMR ($CDCl_3$) τ 2.28–3.18 (m, 17 H, arom), 7.72 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) 142.1, 141.9, 140.8, 140.0, 139.5, 136.9, 130.4, 129.8, 128.7, 127.8, 127.7, 127.4, 127.3, 127.1, 126.5, 126.3, 126.1, 21.3 ppm; IR ($CHCl_3$) 3.28, 3.31, 3.39, 3.44, 3.50, 6.25, 6.72, 6.87, 6.97, 7.25, 8.48, 8.65, 9.28, 9.69, 9.90, 11.11, 13.08, 13.66, 14.29 μm; UV (95% EtOH) 242 nm (ϵ 29998), 256 (20321); MS, m/e 320.1563 (calcd for $C_{25}H_{20}$, m/e 320.1565).

Anal. Calcd for $C_{25}H_{20}$: C, 93.69; H, 6.31. Found: C, 93.58; H, 6.47.

2-Methyl-3,4,6-triphenyl-2-cyclohexen-1-one. To a 75-mL methanolic solution of 6.50 g (31.3 mmol) of 1,2-diphenyl-2-propen-1-one[28a,38] and 4.60 g (31.3 mmol) of 1-phenyl-2-butanone[37] was added a 25-mL methanol solution of sodium methoxide, prepared from 0.75 g (32.6 mmol) of sodium. The solution was refluxed for 3 h and then acidified with 5 mL of glacial acetic acid. The methanol was removed in vacuo and the residue taken up in water and ether extracted. The extract was washed with water, saturated sodium bicarbonate, and saturated sodium chloride, dried over anhydrous magnesium sulfate, concentrated in vacuo, and crystallized from ether/hexane. The yield was 5.39 g (15.9 mmol, 51.0%) of pure 2-methyl-3,4,6-triphenyl-2-cyclohexen-1-one, mp 140–142 °C. The spectral data were as follows: NMR ($CDCl_3$) τ 2.67–3.11 (m, 15 H, arom), 5.92 (m, 1 H, CH), 6.32 (dd, J = 4.0, 14.0 Hz, 1 H, CH), 7.13 (ddd, J = 4.0, 14.0, 14.0 Hz, 1 H, CH), 7.74 (dt, J = 2.0, 14.0 H, 1 H, CH), 8.13 (s, 3 H, CH_3); IR ($CHCl_3$) 3.24, 3.27, 3.30, 3.39, 3.43, 3.50, 6.00, 6.17, 6.25, 6.69, 6.90, 7.25, 7.41, 7.52, 8.13, 8.20, 8.83, 9.28, 9.66, 9.95, 13.16, 14.18 μm; MS, m/e 338.1668 (calcd for $C_{25}H_{22}O$, m/e 338.1671).

Anal. Calcd for $C_{25}H_{22}O$: C, 88.73; H, 6.54. Found: C, 88.65; H, 6.55.

2-Methyl-3,4,6-triphenyl-2-cyclohexen-1-ol. A 0 °C, 25-mL, 1:1 ether/tetrahydrofuran solution of 2.5 g (7.40 mmol) of 2-methyl-3,4,6-triphenyl-2-cyclohexen-1-one was treated with a 10-mL tetrahydrofuran slurry of 0.19 g (5.00 mmol) of lithium aluminum hydride. The mixture was stirred for 5 h with gradual warming to room temperature before, being cautiously quenched with 5 mL of water followed by 5 mL of 10% sodium hydroxide. The precipitate was filtered and the filtrate was concentrated under vacuum to give 2.6 g (7.65 mmol, 103%) of a yellow oil which crystallized upon standing. Recrystallization from ether/hexane afforded 2.4 g (7.06 mmol, 95.4%) of pure 2-methyl-3,4.6-triphenyl-2-cyclohexen-1-ol as a white powder, mp 134–135 °C. The spectra were as follows: NMR ($CDCl_3$) τ 2.68–3.04 (m, 15 H, arom), 5.74 (d, J = 8.0 Hz, 1 H, CH), 6.13 (m, 1 H, CH), 7.05 (tm, J = 12.0 Hz, 1 H, CH), 7.48 (ddd, J = 5.0, 12.0, 12.0 Hz, 1 H, CH), 7.92–8.24 (m, 2 H, CH, OH), 8.20 (s, 3 H, CH_3); IR ($CHCl_3$) 2.80, 3.28, 3.32, 3.44, 3.51, 6.25, 6.71, 6.91, 9.31, 9.52, 9.62, 9.78, 9.99, 10.10, 13.16, 13.89 μm; MS, m/e 340.1882 (calcd for $C_{25}H_{24}O$, m/e 340.1827).

Anal. Calcd for $C_{25}H_{24}O$: C, 88.19; H, 7.11. Found: C, 88.22;, H, 7.15.

3-Methyl-1,4,5-triphenyl-1,3-cyclohexadiene. A 40-mL benzene solution of 2.0 g (5.88 mol) of 2-methyl-3,4,6-triphenyl-2-cyclohexen-1-ol and 50 mg of *p*-toluenesulfonic acid was refluxed for 12 h, cooled, washed with saturated sodium bicarbonate and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated under vacuum to give 1.75 g (5.43 mmol, 92.4%) of pure 3-methyl-1,4,5-triphenyl-1,3-cyclohexadiene as a light-yellow oil. The spectral data were as follows: NMR ($CDCl_3$) τ 2.53–3.12 (m, 15 H, arom), 3.65 (d, J = 2.0 Hz, 1 H vinyl), 6.16 (dd, J = 4.0, 8.0 Hz, 1 H, CH), 6.79 (ddd, A o f AB, J = 2.0, 8.0, 18.0 Hz, 1 H, CH), 7.16 (dd, B of AB, J = 4.0, 18.0 Hz, 1 H, CH), 8.06 (s, 3 H, CH_3); IR (thin film) 3.26, 3.28, 3.32, 3.39, 3.43, 3.50, 3.56, 6.25, 6.71, 6.91, 8.20, 9.30, 9.66, 10.96, 13.12, 13.66, 14.27 μm; MS, m/e 322.1718 (calcd for $C_{25}H_{22}$, m/e 322.1721).

Anal. Calcd for $C_{25}H_{22}$: C, 93.16; H, 6.84. Found: C, 92.92; H, 6.84.

2,3,5-Triphenyltoluene. A mixture of 595 mg (1.85 mmol) of 3-methyl-1,4,5-triphenyl-1,3-cyclohexadiene, 50 mg of 10% palladium on carbon, and 6 mL of decalin was refluxed for 24 h, filtered, concentrated in vacuo, and chromatographed on a 15 cm × 1.0 cm silica gel column. Elution with hexane in 50-mL fractions gave the following: 1–2, 0.97 g of decalin; 3–10, 528 mg (1.65 mmol, 89.2%) of 2,3,5-triphenyltoluene. The physical and spectral data were superimposable with those of the bromination–dehydrohalogenation product from 2-methyl-1,4,6-triphenyltricyclo-[2.2.0.0^{2,6}]hexane.

Ozone Degradation of 2-Methyl-1,4,6-triphenyltricyclo-[2.2.0.0^{2,6}]hexane. A −78 °C, 200-mL methanol solution of 322 mg (1.00 mmol) of 2-methyl-1,4,6-triphenyltricyclo[2.2.0.0^{2,6}]-hexane was treated for 8 min with ozone, passed as a fine stream (0.30 mmol/min from a Welsbach Ozonator) through a fritted gas inlet into the solution. The reaction was allowed to stand for 10 min, excess ozone was removed on a stream of nitrogen, 1.70 g (2.00 mL, 27.2 mmol) of dimethyl sulfide was added, and the mixture was warmed to room temperature. The solution was poured into water and ether extracted, the organic layer was washed with water and saturated sodium chloride, dried over anhydrous sodium sulfate, and concentrated in vacuo to give 344 mg of a light-yellow oil. Spectral analysis and a starch iodine test indicated that the product contained several components including some stable peroxide compounds.

The mixture was treated with 0.53 g (2.00 mmol) of triphenylphosphine in refluxing hexane for 1 h. The reaction was cooled, concentrated in vacuo, and purified on a 20 cm × 20 cm thick layer plate eluted twice with 25% ether in hexane to afford one major band (R_f 0.22) in addition to recovered triphenylphosphine and triphenylphosphine oxide. Workup of this band afforded 227 mg (0.61 mmol, 61.4%) of 3-benzoyl-1,3-diphenyl-1,5-hexadione as a white crystalline powder following recrystallization from *tert*-butyl alcohol, mp 141–142 °C. The spectral data were as follows: NMR ($CDCl_3$) τ 2.08 (m, 2 H, arom), 2.28–2.88 (m, 13 H, arom), 5.43 (d, A of AB q, J = 18.0 Hz, 1 H, CH), 6.01 (d, A of AB q, J = 20.0 Hz, 1 H, CH), 6.18 (d, B of AB q, J = 18.0 Hz, 1 H, CH), 6.60 (d, B of AB q, J = 20.0 Hz, 1 H, CH), 8.12 (s, 3 H, CH_3); ^{13}C NMR (C_6D_6) 206.3, 201.2, 198.4, 140.9, 138.8, 137.9, 132.7, 130.8, 129.2, 129.1, 128.4, 128.2, 127.9, 127.6, 127.5, 127.2, 54.9, 48.1, 43.5, 30.8 ppm; IR ($CHCl_3$) 3.26, 3.28, 3.31, 3.40, 3.44, 5.84, 5.95, 6.27, 6.35, 6.70, 6.92, 7.09, 7.35, 7.87, 8.23, 8.47, 9.98, 10.93, 13.19, 13.61, 14.29, 15.43 μm; UV (95% EtOH) 242 nm (ϵ 11000); MS, m/e 370.1569 (calcd for $C_{25}H_{22}O_3$, m/e 370.1569).

Anal. Calcd for $C_{25}H_{22}O_3$: C, 84.75; H, 6.21. Found: C, 84.10; H, 5.96.

Silver Ion Degradation of 2-Methyl-1,4,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane. In accordance with the method of Padwa et al.[6] 100 mg (0.32 mmol) of 2-methyl-1,4,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane was stirred for 8 h at 25 °C in the absence of light with 10 mL of 9:1 methanol/water containing 100 mg (0.60 mmol) of silver nitrate and then poured into water and ether

(37) (a) Gilsdorf, R. T.; Nord, F. F. *J. Am. Chem. Soc.* **1952**, *74*, 1837–1843. (b) Ivanov, D. *Bull Soc. Chem. Fr.* **1937**, *4*, 682–686.
(38) Fiesselmann, H.; Ribka, *J. Chem. Ber.* **1956**, *89*, 27–39.

extracted. The extract was washed with water and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo to afford 102 mg of a yellow oil. Chromatography on a 20 cm × 20 cm thick layer plate eluted 3 times with 5% ether in hexane afforded two major bands. The first band (R_f 0.74) yielded 27 mg of an unidentified oil. Band 2 (R_f 0.28) gave 63 mg (0.19 mmol, 60%) of pure 4-benzoyl-2-methyl-1,4-diphenylcyclopentene as a light-yellow oil which crystallized upon standing, mp 94–95 °C. The spectra were as follows: NMR ($CDCl_3$) τ 2.45 (m, 2 H, arom), 2.67–3.07 (m, 13 H, arom), 6.28 (d, A of AB q, J = 18.0 Hz, 1 H, CH), 6.46 (d, A of AB q, J = 16.0 Hz, 1 H, CH), 6.85 (d, B of AB q, J = 16.0 Hz, 1 H, CH), 7.14 (d, B of AB q, J = 18.0 Hz, 1 H, CH), 8.18 (s, 3 H, CH_3); ^{13}C NMR (C_6D_6) 200.2, 150.9, 146.6, 138.1, 136.8, 132.9, 132.0, 131.8, 134.4, 129.2, 128.5, 128.2, 128.0, 127.5, 126.7, 125.8, 60.6, 51.3, 48.6, 15.0 ppm; IR (thin film) 3.29, 3.33, 3.40, 3.45, 3.53, 5.99, 6.29, 6.72, 6.94, 7.95, 8.12, 8.47, 9.74, 13.12, 13.72, 14.29 μm; UV (95% EtOH) 244 nm (ϵ 19457), 268 (7726); MS, m/e 338.1671 (calcd for $C_{25}H_{22}O$, m/e 338.1671).

Anal. Calcd for $C_{25}H_{22}O$: C, 88.73; H, 6.54. Found: C, 88.83; H, 6.68.

Ozone Degradation of 4-Benzoyl-2-methyl-1,4-diphenylcyclopentene. The ozonolysis of 48 mg (0.14 mmol) of 4-benzoyl-2-methyl-1,4-diphenylcyclopentene was carried out similarly[28a] to the previous case, using 0.75 mmol of ozone with 10 min standing, 0.42 g (0.50 mL, 6.80 mmol) of dimethyl sulfide being subsequently added. Triphenylphosphine (74 mg, 0.28 mmol) treatment was used as before. Chromatography afforded one major band (R_f 0.20). The material in this band was identical in every respect (melting point, mixed melting point, ^{13}C NMR , TLC, NMR, IR, UV, MS, elemental analysis) with the 3-benzoyl-1,3-diphenyl-1,5-hexanedione isolated from the ozone/triphenylphosphine treatment of 2-methyl-1,4,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane.

Ozone Degradation of 3-Methyl-1,2,5-triphenylbicyclo[3.1.0]hex-2-ene. Ozonolysis of 151 mg (0.47 mmol) of this compound was carried out[28a] in similar fashion to that of the preceding degradation except that the triphenylphosphine treatment was not required. Here 0.90 mmol of ozone was used with a 5-min reaction time to give 162 mg of a light-yellow oil. Dimethyl sulfide (0.85 g, 13.6 mmol) was used in the workup. Chromatography on a 20 cm × 20 cm thick layer plate eluted 5 times with 5% ether in hexane gave the following: band 1, R_f 0.75, 78.0 mg (0.22 mmol, 46.9%) of 1,2,4-triphenyl-4-heptene-1,6-dione, mp 102–103 °C; band 2, R_f 0.69, 16.3 mg (0.05 mmol, 9.7%) of *cis*-2-acetonyl-1-benzoyl-1,2-diphenylcyclopropane as a light-yellow oil.

The spectral data for 1,2,4-triphenyl-4-heptene-1,6-dione were as follows: NMR ($CDCl_3$) τ 2.26 (m, 2 H, arom), 2.60–3.20 (m, 13 H, arom), 3.81 (s, 1 H, vinyl), 5.21 (t, J = 7.0 Hz, 1 H, CH), 6.43 (d, J = 7.0 Hz, 1 H, CH_2), 7.95 (s, 3 H, CH_3); ^{13}C NMR (C_6D_6) 198.5, 197.2, 155.9, 142.4, 139.1, 137.3, 132.5, 129.0, 128.9, 128.8, 128.7, 128.5, 128.0, 127.5, 127.3, 127.1, 53.5, 35.6, 31.5 ppm; IR (thin film) 3.23, 3.25, 3.27, 3.30, 3.42, 5.95, 6.27, 6.37, 6.71, 6.90, 7.36, 7.80, 7.94, 8.26, 8.46, 9.26, 9.71, 9.80, 9.97, 10.20, 10.53, 11.70, 12.64, 13.14, 14.20, 14.95 μm; UV (95% EtOH) 248 nm (ϵ 14168), 264 (10182); MS, m/e 354.1624 (calcd for $C_{25}H_{22}O_2$, m/e 354.1620).

Anal. Calcd for $C_{25}H_{22}O_2$: C , 84.74; H, 6.21. Found: C, 84.49; H, 6.25.

The spectral data for *cis*-2-acetonyl-1-benzoyl-1,2-diphenylcyclopropane were as follows: NMR ($CDCl_3$) τ 2.12 (dd, J = 2.0, 8.0 Hz, 2 H, arom), 2.61–3.27 (m, 13 H, arom), 7.50 (d, A of AB q, J = 6.0 Hz, 1 H, CH), 7.80 (d, J = 4.0 Hz, 1 H, cyclopropyl), 7.80 (d, J = 4.0 Hz, 1 H, cyclopropyl), 8.14 (d, B of AB q, J = 6.0 Hz, 1 H, CH), 8.26 (s, 3 H, CH_3); ^{13}C NMR (C_6D_6) 204.8, 197.6, 139.8, 137.0, 136.7, 132.5, 129.8, 129.5, 129.0, 128.8, 128.4, 128.2, 128.0, 127.5, 126.8, 126.5, 124.6, 52.1, 44.0, 35.8, 30.2, 23.0 ppm; IR (thin film) 3.26, 3.28 3.32, 3.39, 3.44, 3.52, 5.88, 6.01, 6.27, 6.35, 6.71, 6.80, 6.92, 7.38, 7.92, 8.51, 8.66, 8.93, 9.35, 9.71, 14.29, 14.71 μm; UV (95% EtOH) 249 nm (ϵ 11098), 268 (5667); MS, m/e 354.1618 (calcd for $C_{25}H_{22}O_2$, m/e 354.1620).

Anal. Calcd for $C_{25}H_{22}O_2$: C, 84.70; H, 6.26. Found: C, 84.40; H, 5.99.

5-Bromo-4-phenyl-3-penten-2-one. A mixture of 4.00 g (25.0 mmol) of 4-phenyl-3-penten-2-one,[28a,39] 4.45 g (25.0 mmol) of *N*-bromosuccinimide, and 50 mg of benzoyl peroxide in 50 mL of carbon tetrachloride was refluxed for 4 h. The solution was cooled rapidly, the succinimide removed by filtration, and the filtrate concentrated in vacuo to yield 3.80 g (15.9 mmol, 79.5%) of NMR-pure 5-bromo-4-phenyl-3-penten-2-one. This material was used directly as further attempts to purify it resulted in extensive decomposition. The spectral data were as follows: NMR (CCl_4) τ 2.40–2.86 (m, 5 H, arom), 3.58 (s, 1 H, CH), 5.18 (s, 2 H, CH_2), 7.78 (s, 3 H, CH_3); IR (thin film) 3.24, 3.26, 3.29, 3.32, 3.36, 5.84, 5.96, 6.27, 6.37, 6.43, 6.72, 6.93, 7.02, 7.05, 7.40, 8.48, 13.07, 14.37, 15.63 μm; MS, m/e 237.9949 (calcd for $C_{11}H_{11}BrO$, m/e 237.9993).

Anal. Calcd for $C_{11}H_{11}BrO$: C, 55.46; H, 4.66. Found: C, 54.89; H, 4.92.

1,2,4-Triphenyl-4-heptene-1,6-dione. To a −78 °C solution of 16 mmol of lithium diisopropylamide (prepared by addition of 10.5 mL of 1.51 M *n*-butyllithium in hexane to 2.24 mL of diisopropylamine in 20 mL of anhydrous tetrahydrofuran) was added a solution of 2.88 g (14.7 mmol) of deoxybenzoin in 20 mL of tetrahydrofuran. The solution was stirred for 15 min before a solution of 3.50 g (14.7 mmol) of 5-bromo-4-phenyl-3-propen-2-one in 10 mL of dry tetrahydrofuran was added. The reaction mixture was slowly warmed to room temperature and stirred 4 h, quenched with saturated ammonium chloride, and ether extracted. The ether layer was washed with water and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo to afford 3.68 g of the crude keto enone. Chromatography on a 100 cm × 2.5 cm silica gel column eluted with 5% ether in hexane then gave 3.32 g (9.38 mmol, 63.5%) of a dark-yellow oil which was recrystallized from methanol to yield 3.18 g (9.00 mmol, 61.2%) of pure 1,2,4-triphenyl-4-heptene-1,6-dione. This material was identical in every respect (melting point, mixed melting point, TLC, NMR, ^{13}C NMR, IR, UV, MS, elemental analysis) with the ozonolysis product from 3-methyl-1,2,5-triphenylbicyclo[3.1.0]hex-2-ene.

2-Oxophenylacetic Acid Tosylhydrazone. A 40-mL methanol solution of 32.0 g (0.21 mol) of 2-oxophenylacetic acid[40] was treated with a hot, 150-mL methanol solution of 40.0 g (0.22 mol) of *p*-toluenesulfonohydrazide containing 3 drops of concentrated hydrochloric acid. The reaction mixture was warmed for 5 min and then stored for 12 h at −20 °C at which time 50 mL of water was added and the flask stored for an additional 12 h. The acid tosylhydrazone was filtered to give 46.4 g (0.14 mol, 67%). Upon concentration of the filtrate and cooling, a second crop was obtained to give, after drying, a total yield of 57.1 g (0.17 mol, 81%) of pure 2-oxophenylacetic acid tosylhydrazone, mp 174–175 °C. The spectral data were as follows: NMR ($CDCl_3$) τ 0.31 (br s, 1 H, COOH),1.34 (br s, 1 H, NH), 2.18 (dd, J = 2.0, 8.0 Hz, 2 H, arom), 2.32–2.84 (m, 7 H, arom), 7.60 (s, 3 H, CH_3); IR (Nujol) 2.74–4.76, 5.85, 6.21, 6.90, 7.25, 7.52, 8.27, 8.62, 9.35, 9.62, 11.49, 12.35, 12.66, 13.16, 14.29, 14.60, 15.15, μm; MS, m/e 318.0668 (calcd for $C_{15}H_{14}N_2O_4S$, m/e 318.0674).

Anal. Calcd for $C_{15}H_{14}N_2O_4S$: C, 56.59; H, 4.44. Found: C, 56.57; H, 4.49.

2-Oxophenylacetyl Chloride Tosylhydrazone. A suspension of 15.0 g (47.1 mmol) of 2-oxophenylacetic acid tosylhydrazone in 60 mL of anhydrous benzene was refluxed with 14.0 g (8.50 mL, 118 mmol) of thionyl chloride until all the solid had dissolved (1.5–2.5 h). The reaction mixture was cooled, filtered through Celite, and concentrated in vacuo. The remaining yellow residue was recrystallized from benzene/hexane to yield 12.1 g (36.0 mmol, 76.3%) of 2-oxophenylacetyl chloride tosylhydrazone as a light-yellow powder, mp 135–136 °C sl dec. The spectra were as follows: NMR ($CDCl_3$) τ 1.38 (br s, 1 H, NH), 2.16 (d, J = 8.0 Hz, arom), 2.40–2.96 (m, 7 H, arom), 7.58 (s, 3 H, CH_3); IR ($CHCl_3$) 3.13, 3.28, 3.33, 5.73, 6.29, 6.71, 6.94, 7.19, 7.40, 8.20, 8.58, 9.26, 11.43, 12.35, 13.98 14.49 μm; MS m/e 336.0341 (calcd for $C_{15}H_{13}ClN_2O_3S$, m/e 336.0335).

Anal. Calcd for $C_{15}H_{13}ClN_2O_3S$: C, 53.57; H, 3.90. Found: C, 53.54; H, 3.87.

4-Hydroxy-2-phenyl-1-pentene. A solution of (2-phenylallyl)magnesium chloride was prepared from 25.0 g (0.16 mol) of 3-chloro-2-phenylpropene and 10.0 g (0.42 mol) of magnesium

(39) Hughes, L. J. (Monsanto) U.S. Patent 3322831 (Cl. 260–590); *Chem. Abstr.* **1967**, *67*, 53893h.

metal in 250 mL of anhydrous tetrahydrofuran.[35] The solution was cooled to 0 °C and a 10-mL tetrahydrofuran solution of 4.00 g (0.13 mol) of freshly distilled acetaldehyde was added. The reaction was stirred for 15 min and then quenched by dropwise addition of 10 mL of saturated ammonium chloride. The precipitate was filtered and washed with tetrahydrofuran and the filtrate was concentrated in vacuo. The oil obtained was chromatographed on a 50 cm × 2.5 cm silica gel column packed with hexane and eluted in 500-mL fractions to give the following: 1–2, 5.8 g of a mixture of 2-phenylpropene and 2,5-diphenyl-1,5-hexadiene; 3–4, 1% ether in hexane, nil; 5–6, 10% ether in hexane, 6.91 g (42.7 mmol, 46.9%) of 4-hydroxy-2-phenyl-1-pentene as a clear oil. The spectral properties were as follows: NMR ($CDCl_3$) τ 2.40–2.96 (m, 5 H, arom), 4.63 (s, 1 H, vinyl), 4.85 (s, 1 H, vinyl), 6.17 (m, 1 H, CH), 7.40 (d, J = 6.0 Hz, 2 H, CH_2), 7.87 (br s, 1 H, OH), 8.85 (d, J = 6.0 Hz, 3 H, CH_3); IR (thin film) 2.96, 3.26, 3.28, 3.31, 3.39, 3.42, 6.17, 6.27, 6.37, 6.71, 6.93, 7.30, 8.93, 9.30, 9.57, 9.76, 10.70, 11.11, 11.90, 12.90, 14.29 μm; MS, m/e 162.1041 (calcd for $C_{11}H_{14}O$, m/e 162.1045).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.43; H, 8.70. Found: C, 81.26; H, 8.78.

1-Methyl-3-phenyl-3-butenyl 2-Diazophenylacetate. The general procedure of House and Blankley[41] was adapted. A 150-mL methylene chloride solution of 8.00 g (23.8 mmol) of 2-oxophenylacetyl chloride tosylhydrazone and 3.84 g (23.8 mmol) of 4-hydroxy-3-phenyl-1-pentene at 0 °C was treated dropwise with 4.80 g (47.5 mmol) of anhydrous triethylamine. The reaction was stirred for 6 h with gradual warming to 25 °C and then concentrated in vacuo to leave a semisolid oily mass. The residue was rapidly chromatographed through a 10 cm × 2.5 cm alumina column with 5% ether in hexane. Concentration of the bright-yellow solution afforded 6.80 g (22.2 mmol, 93.4%) of 1-methyl-3-phenyl-3-butenyl 2-diazophenylacetate. The spectral data were as follows: NMR ($CDCl_3$) τ 2.58–3.12 (m, 10 H, arom), 4.76 (s, 1 H, vinyl), 4.90 (m, 1 H, CH), 4.96 (s, 1 H, vinyl), 7.28 (dAB q, J = 7.0, 14.0 Hz, 2 H, CH_2), 8.78 (d, 3 H, CH_3); IR (thin film) 3.25, 3.28, 3.31, 3.38, 3.42, 4.81, 5.88, 6.15, 6.27, 6.39, 6.69, 6.90, 7.33, 7.49, 7.78, 8.00, 8.58, 9.48, 9.90, 10.99, 12.85, 13.33, 14.08, 14.60 μm; MS, m/e 306.1359 (calcd for $C_{19}H_{18}N_2O_2$, m/e 306.1568).

Anal. Calcd for $C_{19}H_{18}N_2O_2$: C, 74.51; H, 5.93. Found: C, 73.99; H, 6.17.

***cis*-2-(2-Hydroxypropyl)-1,2-cyclopropane-1-carboxylic Acid Lactone.** The following procedure is a modification of the method of House and Blankley.[41] To 200 mL of refluxing anhydrous benzene suspension of 6.60 g of copper–bronze (LUCO, No. 16, 99.5% copper, Leo Uhlfelder Co., Mt. Vernon, NY) was added dropwise a solution of 6.60 g (21.6 mmol) of 1-methyl-3-phenyl-3-butenyl 2-diazophenylacetate in 50 mL of benzene during 8 h. The mixture was refluxed for an additional 1 h, then cooled, filtered through Celite, and concentrated under vacuum to afford 6.51 g of a yellow oil which crystallized upon standing. Recrystallization from chloroform/hexane then gave 5.11 g (18.4 mmol, 85.1%) of pure *cis*-2-(2-hydroxypropyl)-1,2-diphenylcyclopropane-1-carboxylic acid lactone, mp 155–156 °C. The spectra were as follows: NMR ($CDCl_3$) τ 2.92 (m, 10 H, arom), 5.43 (m, 1 H, CH), 7.65 (m, 2 H, CH_2), 7.70 (s, 2 H, cyclopropyl CH_2), 8.57 (d, J = 6.0 Hz, 3 H, CH_3); IR ($CHCl_3$) 3.25, 3.28, 3.31, 3.37, 3.41, 5.81, 6.25, 6.33, 6.69, 6.78, 6.90, 7.19, 7.34, 7.53, 7.72, 8.06, 8.33, 8.51, 8.68, 8.93, 9.26, 9.35, 9.62, 9.80, 10.00, 10.82, 12.82, 13.16, 14.29, 14.79, 16.00 μm; MS, m/e 278.1300 (calcd for $C_{19}H_{18}O_2$, m/e 278.1306).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.97; H, 6.52. Found: C, 81.96; H, 6.54.

***cis*-1-Benzoyl-2-(2-hydroxypropyl)-1,2-diphenylcyclopropane.** To a 15-mL anhydrous tetrahydrofuran solution of 1.00 g (3.58 mmol) of *cis*-2-(2-hydroxypropyl)-1,2-diphenylcyclopropane-1-carboxylic acid lactone at −78 °C was added 5.00 mL of 1.21 M ethereal phenyllithium (0.50 g, 6.06 mmol). The reaction mixture was stirred for 2.5 h at −78 °C and inversely quenched with saturated ammonium chloride at low temperature. The layers were separated, the aqueous phase was washed with ether, and the extract was washed with water and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo to afford 1.48 g of a yellow oil. Recrystallization from benzene/hexane at 0 °C afforded 1.12 g (3.15 mmol, 88.0%) of pure *cis*-1-benzoyl-2-(2-hydroxypropyl)-1,2-diphenylcyclopropane, mp 124–125 °C. The spectral data were as follows: NMR ($CDCl_3$) τ 1.95 (dd, J = 2.0, 8.0 Hz, 2 H, arom), 2.44–3.18 (m, 13 H, arom), 6.44 (m, 1 H, CH), 7.42 (m, 2 H, 2 CH), 8.12 (d, J = 6.0 Hz, 1 H, CH), 8.50 (br s, 1 H, OH), 8.81 (m, 1 H, CH), 9.03 (d, J = 6.0 Hz, 3 H, CH_3); IR ($CHCl_3$) 2.90, 3.26, 3.28, 3.31, 3.38, 3.42, 3.50, 5.99, 6.25, 6.34, 6.68, 6.90, 7.59, 7.72, 7.87, 8.66, 8.77, 9.26, 9.68, 9.92, 10.36, 12.58, 12.90, 13.16, 14.18 μm; m/e 356.1778 (calcd for $C_{25}H_{24}O_2$, m/e 356.1776).

Anal. Calcd for $C_{25}H_{24}O_2$: C, 84.23; H, 6.79. Found: C, 84.15; H, 6.78.

***cis*-2-Acetonyl-1-benzoyl-1,2-diphenylcyclopropane.** A modification of the oxidation procedure of Corey and Schmidt[42] was employed. A mixture of 1.00 g (2.81 mmol) of *cis*-1-benzoyl-2-(2-hydroxypropyl)-1,2-diphenylcyclopropane and 15.8 g (42.2 mmol) of pyridinium dichromate[42] in 25 mL of anhydrous dimethylformamide was stirred at 25 °C for 12 h. The reaction was diluted with water and ether extracted. The ether layer was washed with water and saturated sodium chloride, dried over anhydrous sodium sulfate, concentrated under vacuum, and rapidly chromatographed on a 20 cm × 20 cm thick layer plate eluted once with 20% ether in hexane to give two major bands. The fast-moving band (R_f 0.96) contained 0.21 g of an unidentified oil. Band 2 (R_f 0.67) afforded 0.66 g (1.87 mmol, 66.6%) of pure *cis*-2-acetonyl-1-benzoyl-1,2-diphenylcyclopropane as a light-yellow oil. The properties of this material were identical in every respect (TLC, NMR, ^{13}C NMR, IR, UV, MS, elemental analysis) with those of the ozone degradation product from 3-methyl-1,2,5-triphenylbicyclo[3.1.0]hex-2-ene.

Control Experiment. Silica Gel Conversion of *cis*-2-Acetonyl-1-benzoyl-1,2-diphenylcyclopropane to 1,2,4-Triphenyl-4-heptene-1,6-dione. A 35-mg (0.10 mol) sample of independently synthesized *cis*-2-acetonyl-1-benzoyl-1,2-diphenylcyclopropane was applied to a 20 cm × 20 cm preparative thick-layer chromatographic plate and allowed to remain in contact with the silica gel for 2 h (a moist slurry of silica gel was determined to have a pH of 6). Elution 4 times with 5% ether in hexane then led to the isolation of 16 mg (0.05 mmol, 45.7%) of 1,2,4-triphenyl-4-heptene-1,6-dione, mp 102–103 °C, and 11 mg (0.03 mmol, 30.5%) of *cis*-2-acetonyl-1-benzoyl-1,2-diphenylcyclopropane.

3-Methyl-2,6-diphenyl-2-cyclohexen-1-one. To a 75-mL 9:1 ether/methanol solution of 1.75 g (32.5 mmol) of sodium methoxide at 0 °C were added a 30-mL ethereal solution of 6.57 g (31.3 mmol) of 1,3-diphenyl-2-propanone and 2.19 g (31.3 mmol) of methyl vinyl ketone during 30 min. The solution was stirred for 8 h with gradual warming to 25 °C and then quenched with 5 mL of glacial acetic acid, diluted with water, and ether extracted. The extract was washed with water, saturated sodium bicarbonate, and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The light-brown oil (8.7 g) was recrystallized from ether/hexane to afford 4.50 g (17.2 mmol, 55%) of pure 3-methyl-2,6-diphenyl-2-cyclohexen-1-one as fluffy white needles, mp 107–108 °C. The spectral data were as follows: NMR ($CDCl_3$) τ 2.64–3.08 (m, 10 H, arom), 6.39 (dd, J = 7.0, 8.0 Hz, 1 H, CH), 7.66 (m, 4 H, 2 CH_2), 8.24 (s, 3 H, CH_3); IR ($CHCl_3$) 3.26, 3.28, 3.33, 3.42, 3.50, 6.02, 6.17, 6.25, 6.69, 7.25, 7.58, 8.20, 8.79, 12.90, 13.25, 14.18, 14.93 μm; MS, m/e 262.1357 (calcd for $C_{19}H_{18}O$, m/e 262. 1355).

Anal. Calcd for $C_{19}H_{18}O$: C, 87.02; H, 6.87. Found: C, 87.13; H, 6.92.

3-Methyl-1,2,6-triphenyl-2-cyclohexen-1-ol. A 20-mL 1:1 ether/tetrahydrofuran solution of 1.50 g (5.73 mmol) of 3-methyl-2,6-diphenyl-2-cyclohexen-1-one was treated with 11.8 mL of 1.21 M ethereal phenyllithium (1.20 g, 14.3 mmol). The reaction was refluxed for 3 h and then poured into saturated ammonium chloride and ether extracted. The organic extract was washed with water and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo to give 4.21 g of a dark-brown oil. Chromatography on a 50 cm × 2.0 cm silica gel column packed in hexane and eluted in 500-mL fractions gave

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(41) House, H. O.; Blankley, C. J. *J. Org. Chem.* **1968**, *33*, 53–60.
(42) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399–402.

the following: 1, hexane, nil; 2–3, 1.04 g of biphenyl; 4, 15% ether in hexane, 0.25 g of an unidentified yellow oil; 5–10, 1.47 g (4.32 mmol, 75.5%) of 3-methyl-1,2,6-triphenyl-2-cyclohexen-1-ol as a yellow oil which crystallized upon standing. Recrystallization from ether/hexane afforded 1.30 g (3.82 mmol, 66.7%) of pure alcohol as a light-yellow powder, mp 149–150 °C. The spectra were as follows: NMR ($CDCl_3$) τ 2.75–3.29 (m, 15 H, arom), 6.65 (dd, J = 2.0, 10.0 Hz, 1 H, CH), 7.61 (m, 3 H, CH_2, OH), 8.15 (m, 2 H, CH_2), 8.45 (s, 3 H, CH_3); IR ($CHCl_3$) 2.83, 2.92, 3.28, 3.30, 3.33, 3.45, 3.52, 3.55, 6.08, 6.29, 6.75, 6.97, 7.35, 7.49, 7.81, 7.98, 8.21, 8.37, 8.51, 8.66, 9.09, 9.26, 9.40, 9.71, 10.00, 10.42, 10.87, 11.11, 13.07, 13.61, 14.39, 15.46 μm; MS, m/e 340.2129 (calcd for $C_{25}H_{24}O$, m/e 340.1825).

Anal. Calcd for $C_{25}H_{24}O$: C, 88.24, H, 7.09. Found: C, 88.30; H, 7.16.

4-Methyl-1,2,3-triphenyl-1,3-cyclohexadiene. A solution of 500 mg (1.47 mmol) of 3-methyl-1,2,6-triphenyl-2-cyclohexen-1-ol and 20 mg of p-toluenesulfonic acid in 25 mL of dry benzene was refluxed for 4 h. The solution was cooled, washed with saturated sodium bicarbonate, and concentrated in vacuo to give 498 mg of a light-yellow solid, mp 96–98 °C. Recrystallization from cyclohexane gave 467 mg (1.45 mmol, 98.6%) of 4-methyl-1,2,3-triphenyl-1,3-cyclohexadiene as a white powder, mp 102–103 °C. The spectral data were as follows: NMR ($CDCl_3$) τ 2.72–3.52 (m, 15 H, arom), 7.32 (m, A of AB, 2 H, CH_2), 7.64 (m, B of AB, 2 H, CH_2), 8.27 (s, 3 H, CH_3); ^{13}C NMR (C_6D_6) 143.7, 143.3, 141.0, 134.7, 130.9, 130.1, 129.6, 129.3, 129.1, 128.4, 127.9, 127.4, 126.6, 126.1, 126.0, 29.5, 28.4, 21.9 ppm; IR ($CHCl_3$) 3.27, 3.29, 3.32, 3.41, 3.50, 3.56, 6.27, 6.37, 6.73, 6.95, 8.23, 9.30, 9.76, 11.05, 13.16, 13.70, 14.49 μm; UV (95% EtOH) 229 nm (ϵ 13 304), 305 (7513); MS, m/e 322.1723 (calcd for $C_{25}H_{22}$, m/e 322.1721).

Anal. Calcd for $C_{25}H_{22}$: C, 93.16; H, 6.84. Found: C, 93.07; H, 6.76.

3-Methyl-1,2,5-triphenylbicyclo[3.1.0]hex-2-ene. A solution of 200 mg (0.62 mmol) of 4-methyl-1,2,3-triphenyl-1,3-cyclohexadiene in 250 mL of deoxygenated cyclohexane was irradiated with a 450-W medium-pressure Hanovia lamp for 90 min through a Pyrex filter at 25 °C and then concentrated to give 203 mg of a mixture of 3-methyl-1,2,5-triphenylbicyclo[3.1.0]hex-2-ene and several unidentified olefinic compounds. Chromatography on a 20 cm × 20 cm thick-layer plate eluted 5 times with hexane gave two major bands. The first broad band (center R_f 0.62) gave 51.0 mg of a complex mixture of unsaturated compounds. The slow-moving band (R_f 0.34) afforded 137 mg (0.43 mmol, 68.6%) of 3-methyl-1,2,5-triphenylbicyclo[3.1.0]hex-2-ene as a white powder, mp 108–109 °C. Recrystallization from methanol resulted in the isolation of 131 mg (0.41 mmol, 65.4%) of the pure bicyclic olefin identical in every respect (melting point, mixed melting point, TLC, NMR, CMR, IR, UV, MS, elemental analysis) with the material isolated from the direct photolysis of 3-methyl-1,2-diphenyl-3-(2-phenylallyl)cyclopropene.

Photolysis Apparatus for Quantum Yield Determinations. All quantum yield determinations were performed with the black box apparatus[36] with light output being measured for each run by a digital electronic actinometer[43] calibrated by ferrioxalate actinometry.[44] The band pass was controlled by a filter solution combination held in a 750-mL total volume three-compartment quartz-faced filter solution cell. The filter solution combination employed in the direct runs was as follows: cell 1, 2.00 M nickel sulfate hexahydrate in 10% sulfuric acid; cell 2, 0.80 M cobalt sulfate heptahydrate in 10% sulfuric acid; cell 3, 0.10 M copper sulfate pentahydrate in 5% sulfuric acid; transmission 0% below 282 nm, 34% at 316 nm, 0% above 348 nm (filter A). The filter solution combination used for the sensitized runs was as follows: cell 1, 0.40 M cobalt sulfate heptahydrate in 10% sulfuric acid; cell 2, 1.00 M copper sulfate pentahydrate in 5% sulfuric acid; cell 3, 0.10 M sodium metavanadate in 0.10 M sodium hydroxide; transmission, 0% below 385 nm, 21% at 406 nm, 0% above 450 nm to 550 nm, gradually rising to 2.5% at 575 nm (filter B).

All quantum yield photolyses were in purified benzene purged with dry deoxygenated nitrogen for 1 h prior to and during photolysis. The glassware used was base treated to minimize complications due to acid-catalyzed reactions of cyclopropenes.

Table II. Direct Quantum Yield Photolyses of 3-Methyl-1,2-diphenyl-3-(2-phenylallyl)cyclopropene (1)

run[a]	% conv	photoproducts, quantum yield (mmol formed) 23	26	7	2
1	8.2	(0.018) 0.082	(0.0050) 0.022	(0.0039) 0.017	(0.0037) 0.016
2	12.8	(0.025) 0.077	(0.0069) 0.022	(0.0051) 0.016	(0.0048) 0.015
3	14.6	(0.030) 0.076	(0.0082) 0.021	(0.0060) 0.015	(0.0057) 0.015
4	17.2	(0.033) 0.075	(0.0092) 0.021	(0.0066) 0.015	(0.0063) 0.014

[a] Runs 1-4 employed 0.373, 0.338, 0.354, and 0.348 mmol of reactant and 0.227, 0.319, 0.389, and 0.439 mEinstein of light, respectively.

Table III. Sensitized Quantum Yields for 3-Methyl-1,2-diphenyl-3-(2-phenylallyl)cyclopropene (1)

run[a]	% conv	photoproducts, quantum yield (mmol formed) 23	26
1	10.6	0.12 (0.0092)	0.19 (0.0151)
2	20.6	0.074 (0.0176)	0.13 (0.0306)
3	23.1	0.071 (0.0225)	0.10 (0.0328)
4	26.9	0.068 (0.0272)	0.090 (0.0360)

[a] Runs 1-4 used 0.299, 0.300, 0.300, and 0.300 mmol of reactant and 0.79, 2.38, 3.18, and 4.01 mEinsteins of light, respectively.

Direct Quantum Yield Results. All direct runs were analyzed by 200-MHz FT NMR, expanded peaks being integrated with a Summagraphics Bit Pad interfaced with a PDP-11/T55 computer. The internal standard employed was 4-methoxybenzophenone. The data are reported in Table II.

Sensitized Quantum Yield Results. All sensitized runs were analyzed as described for the direct runs with 4-methoxybenzophenone as the internal standard. The sensitizer used was p-(dimethylamino)benzophenone (enough to absorb >99% of the light) recrystallized 4 times from methanol. The sensitizer was removed prior to analysis of each run by rapidly filtering the concentrated photolysate through a pad of silica gel with hexane and concentrating the filtrate. The data are reported in Table III.

Control Experiment. Direct Photolysis of 2-Methylene-4-methyl-5,6-diphenyltetracyclo[5.4.0.0^{1,5}.0^{4,6}]undeca-8,10-diene. A 250-mL deoxygenated benzene solution of 115 mg (0.36 mmol) of 2-methylene-4-methyl-5,6-diphenyltetracyclo-[5,4,0,0^{1,5}.0^{4,6}]undeca-8,10-diene was irradiated through filter A on the black box apparatus[36] for 5.08 h (5.65 mEinsteins, 40% conversion). Concentration in vacuo without heat afforded 121 mg of a yellow oil which was analyzed spectrally to contain a 5:1 mixture of tetracyclic starting material/3-methyl-1,2-diphenyl-3-(2-phenylallyl)cyclopropene along with trace amounts of secondary products deriving from the allylcyclopropene. Extensive decomposition of the starting material also occurred owing to the prolonged irradiation conditions. Chromatography on a 20 cm × 20 cm preparative thick-layer plate eluted 6 times with hexane afforded the following: band 1, 68 mg (0.21 mmol, 58.6%) of unreacted tetracyclic, mp 127–128 °C; band 2, 17 mg (0.05 mmol, 14.7%) of cyclopropene. From this it can be estimated that the quantum yield for tetracyclic cycloreverting to allylcyclopropene is $<1.00 \times 10^{-3}$.

Control Experiment. Direct Photolysis of 2-Methyl-1,4,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane. A 250-mL degassed benzene solution of 172 mg (0.53 mmol) of 2-methyl-1,4,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane was photolyzed through filter A for 2.04 h (7.44 mEinsteins, 0% conversion) on the black box apparatus[36] and then concentrated in vacuo at 25 °C to give 173 mg of a yellow oil. Chromatography on a 20 cm × 20 cm thick-layer plate eluted 5 times with hexane afforded one band which

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(44) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

proved to be 156 mg (0.48 mmol, 90.6%) of unreacted 2-methyl-1,4,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane.

Control Experiment. Direct Photolysis of 3-Methyl-1,2,5-triphenylbicyclo[3.1.0]hex-2-ene. A 100-mL solution of 25 mg (0.08 mmol) of 3-methyl-1,2,5-triphenylbicyclo[3.1.0]hex-2-ene in oxygen-free benzene was irradiated for 2.5 h (4.94 mEinsteins, 0% conversion) through filter A on the black box apparatus.[36] Concentration at reduced pressure without heat and purification on a 20 cm × 10 cm thick-layer plate gave 20.6 mg (0.06 mmol, 82.0%) of unchanged bicyclic, mp 108–109 °C.

Control Experiment. Direct Photolysis of 2-Methyl-1,3-diphenyl-3-(2-phenylallyl)cyclopropene. A 750-mL deoxygenated benzene solution of 512 mg (1.59 mmol) of 2-methyl-1,3-diphenyl-3-(2-phenylallyl)cyclopropene was irradiated for 4.75 h (6.21 mEinsteins, 0% conversion) through filter A on the black box apparatus.[36] Concentration under vacuum at 25 °C and chromatography on 20 cm × 20 cm thick-layer plates eluted 4 times with hexane resulted in the reisolation of 459 mg (1.43 mmol, 89.6%) of unreacted starting material as the only eluting band.

Control Experiment. Sensitized Photolysis of 2-Methylene-4-methyl-5,6-diphenyltetracyclo[5.4.0.0^{1,5}.0^{4,6}]-undeca-8,10-diene. A 250-mL degassed benzene solution of 172 mg (0.54 mmol) of 2-methylene-4-methyl-5,6-diphenyltetracyclo[5.4.0.0^{1,5}.0^{4,6}]undeca-8,10-diene and 2.34 g (10.4 mmol) of *p*-(dimethylamino)benzophenone was irradiated for 1.17 h (15.0 mEinsteins, 33% conversion) through filter B on the black box apparatus.[36] The sensitizer (2.32 g, 10.3 mmol, 99.1%) was removed by filtering the concentrated photolysate through silica gel with hexane. The residue recovered from the hexane filtrate was then separated on a 20 cm × 20 cm preparative thick-layer plate eluted 5 times with hexane to give the following: band 1, 108 mg (0.34 mmol, 62.9%) of unreacted starting material, mp 127–128 °C; band 2, 48.3 mg (0.15 mmol, 28.5%) of 2-methyl-1,4,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane. From this the overall quantum yield for the two-photon process required to transform the tetracyclic into the tricyclic is estimated to be 1.02×10^{-2}.

Control Experiment. Sensitized Photolysis of 2-Methyl-1,4,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane. A 250-mL oxygen-purged benzene solution of 330 mg (0.93 mmol) of 2-methyl-1,4,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane and 2.02 g (8.97 mmol) of *p*-(dimethylamino)benzophenone was photolyzed through filter B for 30 min (4.10 mEinsteins, 32% conversion) on the black box apparatus.[36] The sensitizer (1.97 g, 8.76 mmol, 98.0%) was separated by filtration of the concentrated photolysate through silica gel with hexane to give one major band in addition to numerous minor decomposition products. Workup of the major band afforded 212 mg (0.66 mmol, 64.2%) of a 30:1 (NMR) mixture of unreacted starting material and 2-methyl-1,3,5-triphenylbicyclo[3.1.0]hex-2-ene. A very crude estimate of the quantum yield of formation for this bicyclic is 5.2×10^{-3}.

2-Methyl-3,6-diphenyl-2-cyclohexen-1-one. By a procedure analogous to that for the preparation of 3-methyl-2,6-diphenyl-2-cyclohexen-1-one, 3.00 g (20.3 mmol) of 1-phenyl-2-butanone[28a,37b] was reacted with 2.68 g (20.3 mmol) of 1-phenyl-2-propen-1-one[45] in the presence of 1.13 g (21.0 mmol) of sodium methoxide at 0 °C. The reaction mixture was stirred as before for 8 h and then refluxed for 1 h and quenched. The 5.2 g of crude enone was chromatographed on a 30 cm × 2.5 cm silica gel column packed in hexane and eluted in 500-mL fractions to give the following: 1, 1% ether in hexane, nil; 2–3, 2.5% ether in hexane, 0.69 g (4.66 mmol) of unreacted 1-phenyl-2-butanone; 4–9, 10% ether in hexane, 2.94 g (11.2 mmol, 55.3%) of 2-methyl-3,6-diphenyl-2-cyclohexen-1-one as a light-yellow oil which crystallized upon standing. Recrystallization from ether/hexane then afforded 2.64 g (10.1 mmol, 49.7%) of the pure enone, mp 62–63 °C. The spectral characteristics were as follows: NMR ($CDCl_3$) τ 2.84–3.32 (m, 10 H, arom), 6.55 (dd, J = 7.0, 8.0 Hz, 1 H, CH), 7.48 (m, 2 H, CH_2), 7.78 (m, 2 H, CH_2), 8.28 (s, 3 H, CH_3); IR ($CHCl_3$) 3.27, 3.32, 3.42, 3.50, 6.02, 6.17, 6.25, 6.71, 6.78, 6.92, 7.27, 7.38, 7.58, 8.16, 9.01, 9.30, 9.71, 11.43, 13.30, 14.29, 14.39 μm; MS, m/e 262.1351 (calcd for $C_{19}H_{18}O$, m/e 262.1355).

Anal. Calcd for $C_{19}H_{18}O$: C, 87.02; H, 6.87. Found: C, 86.85; H, 7.03.

(45) Reich, H. J.; Reich, I. L.; Renga, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 5434–5447.

2-Methyl-1,3,6-triphenyl-2-cyclohexen-1-ol. By a procedure identical with that for the preparation of 3-methyl-1,2,6-triphenyl-2-cyclohexen-1-ol, 1.50 g (5.73 mmol) of 2-methyl-3,6-diphenyl-2-cyclohexen-1-one was treated with 2.5 equiv of phenyllithium to afford 4.06 g of the crude alcohol. Chromatography on a 50 cm × 2.5 cm silica gel column packed with hexane and eluted in 500-mL fractions gave the following: 1, nil; 2–3, 1% ether in hexane, 1.30 g of biphenyl; 4–6, 10% ether in hexane, 0.31 g of an unidentified orange oil; 7–12, 15% ether in hexane, 1.12 g (3.29 mmol, 57.5%) of a yellow oil which crystallized upon standing. Recrystallization from ether/hexane afforded 1.01 g (2.97 mmol, 51.8%) of pure 2-methyl-1,3,6-triphenyl-2-cyclohexen-1-ol, mp 118–119 °C. The spectra were as follows: NMR ($CDCl_3$) τ 2.60–3.32 (m, 15 H arom), 6.80 (dd, J = 2.0, 11.0 Hz, 1 H, CH), 7.49 (m, 3 H, CH_2, OH), 8.08 (m, 2 H, CH_2), 8.69 (s, 3 H, CH_3); IR ($CHCl_3$) 2.83, 2.94, 3.29, 3.33, 3.41, 3.45, 3.51, 6.29, 6.76, 6.95, 7.30, 7.52, 7.97, 8.25, 8.55, 8.66, 9.52, 9.82, 10.05, 10.47, 13.55, 14.66 μm; MS, m/e 340.1828 (calcd for $C_{25}H_{24}O$, m/e 340.1826).

Anal. Calcd for $C_{25}H_{24}O$: C, 88.24; H, 7.09. Found: C, 88.09; 7.18.

3-Methyl-1,2,4-triphenyl-1,3-cyclohexadiene. By a procedure identical with that reported for the preparation of 4-methyl-1,2,3-triphenyl-1,3-cyclohexadiene, 500 mg (1.47 mmol) of 2-methyl-1,3,6-triphenyl-2-cyclohexen-1-ol was converted to 454 mg (1.41 mmol, 95.9%) of pure 3-methyl-1,2,4-triphenyl-1,3-cyclohexadiene, mp 104–105 °C. The spectral data were as follows: NMR ($CDCl_3$) τ 2.62–3.26 (m, 15 H, arom), 7.36 (m, 4 H, 2 CH_2), 8.50 (s, 3 H, CH_3); ^{13}C NMR (C_6D_6) 143.5, 143.2, 141.0, 134.6, 130.8, 130.1, 129.6, 129.3, 129.0, 128.7, 128.4, 127.9, 127.8, 127.4, 126.6, 126.4, 126.0, 31.3, 30.6, 18.4 ppm; IR ($CHCl_3$) 3.26, 3.27, 3.31, 3.44, 3.49, 3.56, 6.25, 6.71, 6.92, 7.91, 9.28, 9.63, 10.96, 13.16, 13.70, 14.35 μm; UV (95% EtOH) 230 nm (ϵ 18740), 308 (10834); MS, m/e 322.1723 (calcd for $C_{25}H_{22}$, m/e 322.1721).

Anal. Calcd for $C_{25}H_{22}$: C, 93.16; H, 6.84. Found: C, 92.91; H, 6.35.

2-Methyl-1,3,5-triphenylbicyclo[3.1.0]hex-2-ene. A solution of 200 mg (0.62 mmol) of 3-methyl-1,2,4-triphenyl-1,3-cyclohexadiene in 250 mL of deoxygenated cyclohexane was irradiated with a 450-W medium-pressure Hanovia lamp for 6 h through a Pyrex filter at 25 °C and then concentrated to give 201 mg of a yellow oil. Chromatography on a 20 cm × 20 cm preparative thick-layer plate eluted 12 times with pentane showed two major bands which analyzed as follows: band 1, R_f 0.76, 107 mg of a complex mixture of unsaturated hydrocarbons; band 2, R_f 0.61, 70 mg (0.22 mmol, 35%) of 2-methyl-1,3,5-triphenylbicyclo-[3.1.0]hex-2-ene, mp 105–106 °C. This material proved identical with that observed in the product mixture from the sensitized irradiation of 2-methyl-1,4,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane.

The spectral data for 2-methyl-1,3,5-triphenylbicyclo[3.1.0]-hex-2-ene were as follows: NMR ($CDCl_3$) τ 2.50–3.20 (m, 15 H, arom), 6.52 (dq, A of AB, J = 1.0, 18.0 Hz, 1 H, CH), 6.90 (dq, B of AB, J = 1.0, 18.0 Hz, 1 H, CH), 7.88 (d, J = 4.0 Hz, 1 H, cyclopropyl), 8.30 (t, J = 1.0 Hz, 3 H, CH_3), 8.98 (d, J = 4.0 Hz, 1 H, cyclopropyl; ^{13}C NMR (C_6D_6) 141.9, 141.6, 138.5, 137.0, 133.9, 129.4, 129.0, 128.9, 127.9, 127.8, 126.4, 126.0, 125.8, 53.6, 49.8, 35.2, 23.4, 14.9 ppm; IR ($CHCl_3$) 3.26, 3.28, 3.31, 3.45, 3.52, 6.25, 6.70, 6.93, 7.26, 9.48, 9.71, 13.61, 14.33 μm UV (95% EtOH) 228 nm (ϵ 13802), 252 (11907), 275 (6224); MS, m/e 322.1778 (calcd for $C_{25}H_{22}$, m/e 322.1721).

Anal. Calcd for $C_{25}H_{22}$: C, 93.16; H, 6.84. Found: C, 93.07; H, 6.97.

Thermal Chemistry Results. All thermolyses were performed in base-washed thick-walled Pyrex tubes sealed under 0.05-mm vacuum. The products were separated by preparative thick-layer chromatography and analyzed spectrally. The results are summarized in Table IV.

Exploratory Direct Photolysis of 2-Methyl-1,3-diphenyl-3-(2-phenylallyl)cyclopropene. A 750-mL degassed benzene solution of 536 mg (1.66 mmol) of 2-methyl-1,3-diphenyl-3-(2-phenylallyl)cyclopropene was photolyzed through filter C (see photolysis apparatus section for spiro cyclopropenes) on the black box apparatus[36] for 8.42 h (6.21 mEinsteins, 28% conversion). Concentration under vacuum without heat afforded 541 mg of a yellow oil. NMR spectral analysis of the crude photolysate indicated the presence of at least eight products. No

Table IV. Thermal Chemistry Results for 2-Methyl- and 3-Methylphenylcyclopropenes 1 and 2 and Related Compounds[a]

reactant	temp, °C	time, h	% isol/ % conv
1	100	0.75	30/39
	120	3.00	95/100
26	140	2.0	47/55
23	120	4.00	90/0
7	120	2.50	82/0
2	100	0.75	43/45
	120	2.5	90/100

[a] The product in all runs was compound 23 except in the run beginning with 7 where 7 was isolated. Runs were made with 0.33, 0.31, 0.12, 0.63, 0.049, 0.36, and 0.21 mmol, respectively.

further attempt was made to separate or assay the product mixture.

Exploratory Sensitized Photolysis of 2-Methyl-1,3-diphenyl-3-(2-phenylallyl)cyclopropene. A 750-mL deoxygenated benzene solution of 471 mg (1.46 mmol) of 2-methyl-1,3-diphenyl-3-(2-phenylallyl)cyclopropene and 4.38 g (19.5 mmol) of *p*-(dimethylamino)benzophenone was irradiated through filter B on the black box apparatus[36] for 25 min (2.96 mEinsteins, 94.7% conversion). The sensitizer (4.31 g, 19.2 mmol, 98.3%) was recovered in the previously described fashion and the photolysate was separated on three 20 cm × 20 cm thick-layer plates eluted 6 times with hexane to give the following: band 1, R_f 0.71, 42.7 mg (0.13 mmol, 9.1%) of 2-methylene-6-methyl-4,5-diphenyltetracyclo[5.4.0.0^{1,5}.0^{4,6}]undeca-8,10-diene; band 2, R_f 0.58, 337 mg (1.05 mmol, 71.6%) of 2-methyl-1,4,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane containing a trace of unreacted 2-methyl-1,3-diphenyl-3-(2-phenylallyl)cyclopropene.

The spectral data for 2-methylene-6-methyl-4,5-diphenyltetracyclo[5.4.0.0^{1,5}.0^{4,6}]undeca-8,10-diene were as follows: NMR ($CDCl_3$) τ 2.64–3.16 (m, 10 H, arom), 3.19 (m, 2 H, 2 vinyl), 3.31 (m, 1 H, vinyl), 3.84 (m, 1 H, vinyl), 5.25 (s, 1 H, vinyl), 5.32 (s, 1 H, vinyl), 6.81 (d, A of AB q, J = 16.0 Hz, 1 H, CH), 7.00 (d, J = 2.0 Hz, 1 H, CH), 7.30 (d, B of AB q, J = 16.0 Hz, 1 H, CH), 0.90 (s, 3 H, CH_3); ^{13}C NMR (acetone-d_6) 158.9, 147.1, 137.4, 134.3, 131.8, 129.7, 129.1, 125.5, 128.4, 127.2, 126.6, 125.5, 123.7, 122.1, 117.3, 56.2, 54.6, 47.2, 44.8, 38.7, 33.9, 15.7 ppm; IR ($CHCl_3$) 3.29, 3.32, 3.36, 3.45, 3.53, 6.07, 6.27, 6.70, 6.94, 7.27, 9.35, 9.73, 9.86, 11.39, 14.49 μm; UV (95% EtOH) 220 nm (ϵ 31 263), 263 (4897), 275 (4627); MS, m/e 322.1717 (calcd for $C_{25}H_{22}$, m/e 322.1721).

Anal. Calcd for $C_{25}H_{22}$: C, 93.16; H, 6.84. Found: C, 93.09; H, 6.76.

Sensitized Quantum Yield Results. All sensitized runs were analyzed as described earlier for the 3-methyl-3-(phenylallyl)-cyclopropene series with 4-methoxybenzophenone as the internal standard. The sensitizer was *p*-(dimethylamino)benzophenone. Workup of the photolysates to remove the sensitizer prior to analysis was performed as described previously. The data are reported in Table V.

1-Benzylidene-4-methyl-4-phenylcyclohexane. A 300-mL anhydrous tetrahydrofuran slurry of 47.4 g (122 mmol) of benzyltriphenylphosphonium chloride was treated with 80.1 mL of a 1.51 M hexane solution of *n*-butyllithium (7.74 g, 121 mmol). The mixture was stirred at 0 °C for 15 min before a 50-mL ether solution of 15.0 g (80.7 mmol) of 4-methyl-4-phenylcyclohexanone[46] was added dropwise during 30 min. The reaction mixture was stirred for 30 min at 0 °C, 30 min at 25 °C, and 2 h at reflux and then quenched with water and ether extracted. The organic layer was washed with water and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo. Chromatography of the semisolid mass on a 100 cm × 3.5 cm silica gel column packed in hexane and eluted in 500-mL fractions gave the following: 1–2, nil; 3–8, 1% ether in hexane, 20.4 g (77.9 mmol, 96.5%) of pure 1-benzylidene-4-methyl-4-phenylcyclohexane as a clear oil. The spectral data were as follows: NMR (CCl_4) τ 2.44–3.02 (m, 10 H, arom), 3.78 (s, 1 H, vinyl), 7.07–8.67 (complex, 8 H, 4 CH_2), 8.79 (s, 3 H, CH_3); IR (thin film) 3.24, 3.27, 3.29, 3.38, 3.41, 3.50, 6.01, 6.23, 6.33, 6.64, 6.80, 6.88, 7.28, 7.46, 7.75, 8.62, 9.07, 9.28, 9.67, 10.47, 10.87, 11.70, 11.85, 12.66, 13.04, 13.51, 14.29 μm; MS, m/e 262.1716 (calcd for $C_{20}H_{22}$, m/e 262.1721).

Anal. Calcd for $C_{20}H_{22}$: C, 91.60; H, 8.40. Found: C, 91.31; H, 8.57.

1-Bromo-1-(1-bromobenzyl)-4-methyl-4-phenylcyclohexane. A solution of 20.0 g (76.3 mmol) of 1-benzylidene-4-methyl-4-phenylcyclohexane in 150 mL of anhydrous ether was treated with 12.2 g (3.93 mL, 76.3 mmol) of bromine dropwise with stirring during 30 min at 25 °C. The reaction mixture was refluxed for 30 min and the ether removed in vacuo to afford 32.1 g (75.9 mmol, 99.5%) of 1-bromo-1-(1-bromobenzyl)-4-methyl-4-phenylcyclohexane as a mixture of isomers. The product was used without further purification. The spectral properties were as follows: NMR (CCl_4) τ 2.37–3.11 (m, 10 H, arom), 4.71 and 5.12 (2 s, 1 H, CH), 7.24–8.69 (complex, 8 H, 4 CH_2), 8.76 and 8.84 (2 s, 3 H, CH_3); IR (thin film) 3.24, 3.27, 3.30, 3.38, 3.41, 3.49, 6.24, 6.33, 6.66, 6.80, 6.90, 6.98, 7.24, 7.34, 7.44, 7.68, 7.81, 7.92, 8.01, 8.26, 8.52, 8.64, 8.93, 9.25, 9.67, 9.78, 10.42, 10.54, 11.51, 12.09, 12.33, 13.05, 14.53, 15.50, 16.42 μm; MS, m/e 420.0096 (calcd for $C_{20}H_{22}Br_2$, m/e 420.0088).

Anal. Calcd for $C_{20}H_{22}Br_2$: C, 56.87; H, 5.21. Found: C, 56.64; H, 5.32.

1-(1-Bromobenzylidene)-4-methyl-4-phenylcyclohexane. A 250-mL ethanol solution of 32.0 g (76.0 mmol) of 1-bromo-1-(1-bromobenzyl)-4-methyl-4-phenylcyclohexane was warmed to 50 °C and treated with a 40-mL ethanolic solution of 6.90 g (123 mmol) of potassium hydroxide. The reaction mixture was stirred for 15 min, quenched with water, and ether extracted. The extract was washed several times with water and once with saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated under vacuum to afford 25.2 g (73.9 mmol, 97.2%) of the crude bromide as a brown oil. Purification by chromatography on a 40 cm × 5 cm silica gel column packed in hexane gave 24.6 g (72.2 mmol, 95.1%) of pure 1-(1-bromobenzylidene)-4-methyl-4-phenylcyclohexane as the only eluted compound. The spectra were as follows: NMR (CCl_4) τ 2.38–3.12 (m, 10 H, arom), 7.04–8.76 (complex, 8 H, 4 CH_2), 8.79 (s, 3 H, CH_3); IR (thin film) 3.25, 3.27, 3.31, 3.38, 3.41, 3.50, 6.24, 6.33, 6.65, 6.80, 6.88, 7.25, 7.88, 7.99, 8.23, 9.07, 9.31, 9.68, 10.46, 11.55, 11.83, 12.67, 13.09, 13.30, 14.33, 15.77 μm; MS, m/e 340.0831 (calcd for $C_{20}H_{21}Br$, m/e 340.0826).

Anal. Calcd for $C_{20}H_{21}Br$: C, 70.38; H, 6.16. Found: C, 70.36; H, 5.98.

2-(4-Methyl-4-phenylcyclohexylidene)-2-phenylacetic Acid. To a refluxing suspension of 0.67 g (28.0 mmol) of powdered magnesium metal in 10 mL of anhydrous tetrahydrofuran was added 2 drops of 1,2-dibromoethane followed by a 40-mL tetrahydrofuran solution of 9.40 g (27.6 mmol) of 1-(1-bromobenzylidene)-4-methyl-4-phenylcyclohexane added dropwise during 1 h. The reaction mixture was refluxed for 2 h and cooled and a large excess of dry ice was gradually added. When all of the dry ice had reacted or sublimed, the reaction mixture was poured into 2% hydrochloric acid and ether extracted. The organic layer was washed with water and saturated sodium chloride, dried over anhydrous sodium sulfate, and concentrated in vacuo to give 7.70 g (25.2 mmol, 91.3%) of pure 2-(4-methyl-4-phenylcyclohexylidene)-2-phenylacetic acid as a viscous clear oil. The spectral data were as follows: NMR (CCl_4) τ −0.80 (br s, 1 H, COOH), 2.50–3.03 (m, 10 H, arom), 6.84–8.72 (complex, 8 H, 4 CH_2), 8.78 (s, 3 H, CH_3); IR (thin film) 2.81–4.46, 5.97, 6.21, 6.27, 6.70, 6.77, 6.84, 6.94, 7.15, 7.28, 7.78, 7.89, 8.03, 8.14, 9.35, 9.73, 10.53, 13.18, 13.72, 14.47, 14.93, 15.41 μm; MS, m/e 306.1611 (calcd for $C_{21}H_{22}O_2$, m/e 306.1619).

Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.35; H, 7.19. Found: C, 82.56; H, 7.43.

1-(4-Methyl-4-phenylcyclohexylidene)-1-phenyl-2-propanone. A 0 °C 20-mL anhydrous ether solution of 7.65 g (25.0 mmol) of 2-(4-methyl-4-phenylcyclohexylidene)-2-phenylacetic acid was treated dropwise with 57.3 mL of a 1.10 M ether solution of methyllithium (1.39 g, 63.0 mmol, 2.5 equiv). The reaction mixture was warmed to 22 °C and stirred for 3 h and then inversely quenched into saturated ammonium chloride and ether extracted. The ether layer was washed with water and

(46) Bordwell, F. G.; Frame, R. R.; Scamehorn, R. G.; Strong, J. G.; Meyerson, S. *J. Am. Chem. Soc.* **1967**, *89*, 6704–6711.

Table V. Sensitized Quantum Yields to 2-Methyl-1,3-diphenyl-3-(2-phenylallyl)cyclopropene (2)

run	reactant light: mmol	reactant light: absorbed, mEinstein	reactant light: % conv	photoproduct, quantum yield (mmol): 23	photoproduct, quantum yield (mmol): 26
1	0.322	0.206	17.5	0.25 (0.051)	0.026 (0.0053)
2	0.332	0.273	20.7	0.22 (0.061)	
3	0.284	0.356	21.8		0.021 (0.0074)
4	0.334	0.398	24.6	0.18 (0.074)	0.020 (0.0078)

saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated under vacuum to yield 7.18 g (23.6 mmol, 93.7%) of essentially pure enone. Silica gel chromatography on a 50 cm × 2.5 cm column eluted with 5% ether in hexane afforded 7.00 g (23.1 mmol, 91.6%) of analytically pure 1-(4-methyl-4-phenylcyclohexylidene)-1-phenyl-2-propanone as the only eluted compound. The spectra were as follows: NMR (CCl_4) τ 2.58–3.08 (m, 10 H, arom), 7.29–8.52 (complex, 8 H, 4 CH_2), 8.12 (s, 3 H, CH_3), 8.80 (s, 3 H, CH_3); IR (thin film) 3.24, 3.27, 3.31, 3.38, 3.42, 3.50, 5.92, 6.25, 6.67, 6.90, 7.26, 7.39, 7.77, 8.00, 8.28, 8.42, 8.55, 8.64, 9.10, 9.34, 9.71, 10.52, 13.14, 14.29 μm; MS, m/e 304.1817 (calcd for $C_{22}H_{24}O$, 304.1827).

Anal. Calcd for $C_{22}H_{24}O$: C, 86.84; H, 7.89. Found: C, 86.04; H, 7.73.

1-(4-Methyl-4-phenylcyclohexylidene)-1-phenyl-2-propanone Tosylhydrazone. To a solution of 6.95 g (22.9 mmol) of 1-(4-methyl-4-phenylcyclohexylidene)-1-phenyl-2-propanone in 30 mL of ethanol was added a 50-mL ethanolic solution of 4.26 g (22.9 mmol) of *p*-toluenesulfonohydrazide containing 0.05 mL of concentrated hydrochloric acid. The mixture was warmed to 40 °C for 5 min, then capped, and stored at −20 °C for 2 days. The white crystals were filtered to give 7.88 g (16.7 mmol, 72.9%) of the tosylhydrazone. A second crop gave an additional 1.01 g (2.14 mmol, 9.3%) making the total yield 8.89 g (18.8 mmol, 82.1%). Recrystallization from ethanol then afforded 8.17 g (17.3 mmol, 75.6%) of pure 1-(4-methyl-4-phenylcyclohexylidene)-1-phenyl-2-propanone tosylhydrazone, mp 150–151 °C sl dec. The spectral data were as follows: NMR ($CDCl_3$) τ 2.05 (d, J = 8.0 Hz, 2 H, arom), 2.40–3.05 (m, 12 H, arom), 7.53 (s, 3 H, CH_3), 7.59–8.76 (complex, 8 H, 4 CH_2), 8.34 (s, 3 H, CH_3), 8.80 (s, 3 H, CH_3); IR ($CHCl_3$) 3.11, 3.25, 3.27, 3.31, 3.33, 3.38, 3.42, 3.50, 6.25, 6.69, 6.83, 6.92, 7.20, 7.46, 7.65, 8.13, 8.41, 8.55, 9.12, 9.28, 9.56, 9.79, 10.42, 10.87, 11.42, 12.21, 14.27, 15.11, 15.87 μm; UV (95% EtOH): 228 nm (ϵ 19309), 242 (16091), 276 (4076), 300 (429); MS, m/e 472.2177 (calcd for $C_{29}H_{32}N_2O_2S$, m/e 472.2184).

Anal. Calcd for $C_{29}H_{32}N_2O_2S$: C, 73.73; H, 6.78; N, 5.93. Found: C, 73.74; H, 6.88; N, 5.76.

***cis*- and *trans*-2,6-Dimethyl-1,6-diphenylspiro[2.5]oct-1-ene.** A vigorously stirred solution of 1.80 g (3.81 mmol) of 1-(4-methyl-4-phenylcyclohexylidene)-1-phenyl-2-propanone tosylhydrazone and 0.60 g (11.1 mmol) of sodium methoxide in 1 L of anhydrous tetrahydrofuran was purged with purified nitrogen for 1 h and then photolyzed through Pyrex until the bright red color of the diazo compound had disappeared (approximately 25 min). Concentration and chromatography on a 20 cm × 20 cm thick-layer plate eluted twice with hexane yielded one fast-moving band which contained 1.04 g (3.61 mmol, 94.8%) of a 1:1 mixture (NMR) of *cis*- and *trans*-2,6-dimethyl-1,6-diphenylspiro[2.5]-oct-1-ene. Separation of the isomers was achieved by high-pressure liquid chromatography on a 35 cm × 0.64 cm silica microbead[29] column eluted with 1% methylene chloride in pentane (100-mg injections, two recycle modes) afforded, after crystallization from methanol, 0.53 g (1.84 mmol, 48.3%) of isomer **1**, mp 76–77 °C, and 0.41 g (1.42 mmol, 37.4%) of isomer **2**, mp 78–79 °C.

The spectral data for isomer 1 were as follows: NMR (CCl_4) τ 2.36–2.94 (m, 10 H, arom), 7.80 (s, 3 H, CH_3), 7.75–8.75 (complex, 8 H, 4 CH_2), 8.68 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) 149.7, 130.6, 128.4, 128.1, 126.9, 125.7, 125.5, 125.2, 124.1, 123.0, 119.3, 39.1, 37.8, 33.1, 30.0, 27.6, 10.5 ppm; IR (CCl_4) 3.27, 3.29, 3.33, 3.45, 3.53, 5.49, 6.01, 6.29, 6.97, 7.31, 7.49, 8.40, 9.11, 9.35, 9.76, 10.64, 14.71 μf; UV (95% EtOH) 213 nm (ϵ 16363), 225 (8291), 274 (14836); MS, m/e 288.1865 (calcd for $C_{22}H_{24}$, m/e 288.1878).

Anal. Calcd for $C_{22}H_{24}$: C, 91.60; H, 8.40. Found: C, 91.31; H, 8.11.

The spectral data for isomer 2 were as follows: NMR (CCl_4) τ 2.40–3.00 (m, 10 H, arom), 7.68 (s, 3 H, CH_3), 7.75–8.75 (complex, 8 H, 4 CH_2), 8.76 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) 147.9, 130.7, 128.5, 128.3, 127.0, 126.1, 125.3, 125.0, 123.6, 39.1, 38.1, 33.2, 30.7, 27.7, 10.7 ppm; IR CCl_4) 3.26, 3.28, 3.32, 3.40, 3.44, 3.52, 5.48, 6.26, 6.71, 6.85, 6.93, 7.26, 7.46, 9.09, 9.27, 9.68, 10.98, 13.14, 14.29 μm; UV (95% EtOH) 211 nm (ϵ 16098), 222 (8428), 271 (13446); MS, m/e 288.1877 (calcd for $C_{22}H_{24}$, m/e 288.1878).

Anal. Calcd for $C_{22}H_{24}$: C, 91.60; H, 8.40. Found: C, 91.29; H, 8.60.

Oxidation of Isomer 1 of 2,6-Dimethyl-1,6-diphenylspiro[2.5]oct-1-ene. A mixture of 2 mL of ether, 2 mL of water, 200 mg (0.69 mmol) of isomer 1 of 2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene, and 10 mg of osmium tetraoxide was stirred vigorously, while a total of 0.32 g (1.46 mmol) of finely powdered sodium metaperiodate was added during a 40-min period. The reaction mixture was stirred for 2 h at 22 °C and then poured into water and ether extracted. The combined organic layers were washed with water, dilute sodium bisulfite, and saturated sodium chloride, dried over anhydrous sodium sulfate, and concentrated in vacuo to give 185 mg (0.58 mmol, 83.4%) of crude diketone as a light-tan oil. Chromatography on a 20 cm × 20 cm thick-layer plate eluted once with 10% ether in hexane yielded one band which proved on workup to be 149 mg (0.47 mmol, 68.1%) of isomer 1 of 1-acetyl-1-benzoyl-4-methyl-4-phenylcyclohexane as a light-yellow oil. Recrystallization from methanol afforded 137 mg (0.43 mmol, 61.6%) of pure diketone, mp 91–92 °C. The spectra were as follows: NMR ($CDCl_3$) τ 2.28 (dd, J = 2.0, 10.0 Hz, 2 H, arom), 2.44–2.92 (m, 8 H, arom), 7.44–8.95 (complex, 8 H, 4 CH_2), 8.08 (s, 3 H, CH_3), 8.95 (s, 3 H, CH_3); IR (thin film) 3.25, 3.27, 3.31, 3.38, 3.42, 3.50, 5.85, 5.98, 6.25, 6.69, 6.87, 7.38, 7.94, 8.06, 8.26, 10.58, 12.74, 13.07, 14.08 μm; MS, m/e 320.1776 (calcd for $C_{22}H_{24}O_2$, m/e 320.1776).

Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.45; H, 7.56. Found: C, 82.42; H, 7.52.

Oxidation of Isomer 2 of 2,6-Dimethyl-1,6-diphenylspiro[2.5]oct-1-ene. A 200-mg (0.69 mmol) sample of isomer **2** of 2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene was oxidized as described for isomer 1. Workup and chromatography as before afforded 155 mg (0.49 mmol, 69.8%) of isomer **2** of 1-acetyl-1-benzoyl-4-methyl-4-phenylcyclohexane as a light-yellow oil. Recrystallization from methanol yielded 139 mg (0.43 mmol, 63%) of the pure diketone, mp 89–90 °C. The spectral data were as follows: NMR ($CDCl_3$) τ 2.28 (dd, J = 2.0, 10.0 Hz, 2 H, arom), 2.44–2.92 (m, 8 H, arom), 7.44–8.95 (complex, 8 H, 4 CH_2), 7.96 (s, 3 H, CH_3), 8.88 (s, 3 H, CH_3); IR (thin film) 3.25, 3.27, 3.31, 3.38, 3.42, 3.50, 5.85, 5.98, 6.25, 6.69, 6.87, 7.38, 7.94, 8.06, 8.26, 10.58, 12.74, 13.07, 14.08 μm; MS, m/e 320.1776 (calcd for $C_{22}H_{24}O_2$, m/e 320.1776).

Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.44; H, 7.56. Found: C, 82.44; H, 7.49.

Selective Equatorial Carbonyl Reduction in Isomer 1 of 1-Acetyl-1-benzoyl-4-methyl-4-phenylcyclohexane. To a 10-mL 0 °C solution of 96 mg (0.30 mmol) of isomer 1 of 1-acetyl-1-benzoyl-4-methyl-4-phenylcyclohexane was added 0.33 mL of a 1.00 M tetrahydrofuran solution of lithium tri-*sec*-butylborohydride (6.27 mg, 0.33 mmol, 1.1 equiv) dropwise with stirring. The reaction mixture was stirred at 0 °C for 1 h, then quenched with saturated ammonium chloride, washed with water and saturated sodium chloride, dried over anhydrous sodium sulfate, and concentrated in vacuo to afford 89.1 mg (0.28 mmol, 92.2%) of a light-yellow oil. Attempted purification resulted in substantial decomposition. Infrared analysis of the crude oil showed predominant acetyl reduction and some benzoyl reduction. NMR showed diminution of the acetyl methyl at τ 8.00 with the appearance of high-field methyl doublets (two isomers) and overlapping methine quartets at τ 6.18. By NMR, it was estimated that acetyl reduction predominated over benzoyl reduction by

65:35. This isomer was thus assigned as the cis isomer.

Selective Equatorial Carbonyl Reduction of Isomer 2 of 1-Acetyl-1-benzoyl-4-methyl-4-phenylcyclohexane. To a 10-mL 0 °C tetrahydrofuran solution of 93 mg (0.29 mmol) of isomer 2 of 1-acetyl-1-benzoyl-4-methyl-4-phenylcyclohexane was added 0.32 mL of a 1.00 M tetrahydrofuran solution of lithium tri-*sec*-butylborohydride (6.08 mg, 0.32 mmol, 1.1 equiv) dropwise with stirring. The reaction was stirred at 0 °C for 1 h and then worked up as per isomer 1 to give 82.7 mg (0.26 mmol, 88.6%) of a light-yellow oil. Spectral analysis of the crude oil indicated predominant benzoyl reduction by ca. 75:25 over acetyl reduction with a decrease in intensity of the carbonyl absorption at 5.98 μm, a decrease in the ortho phenyl NMR resonances, and the appearance of two singlets (two isomers) at τ 5.14 and 5.36 for the hydroxy-benzyl methine.

Exploratory Direct Photolysis of *cis*-2,6-Dimethyl-1,6-diphenylspiro[2.5]oct-1-ene. A 250-mL solution of 102 mg (0.35 mmol) of *cis*-2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene in deoxygenated cyclohexane was irradiated for 52 min (1.54 mEinsteins, 42% conversion) through filter C on the black box apparatus.[36] Concentration of the photolysate without heat and separation by high-pressure liquid chromatography on a 35 cm X 0.64 cm porous silica microbead[29] column in two 55-mg injections eluted through two recycle modes with 1% methylene chloride in pentane afforded the following: 1, 54 mg (0.19 mmol, 54.3%) of *cis*-2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene; 2, 31.5 mg (0.11 mmol, 31.4%) of *trans*-2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene; 3, 6.9 mg (0.02 mmol, 5.7%) of 4-methyl-1-(*cis*-2-methyl-1-phenylethenyl)-4-phenyl-1-cyclohexene.

The spectral data for 4-methyl-1-(*cis*-2-methyl-1-phenylethenyl)-4-phenyl-1-cyclohexene were as follows: NMR ($CDCl_3$) τ 2.52–3.05 (m, 10 H, arom), 4.32 (q, J = 7.0 Hz, 1 H, vinyl), 4.69 (t, J = 2.0 Hz, 1 H, vinyl), 7.28–8.90 (complex, 6 H, 3 CH_2), 8.55 (d, J = 7.0 Hz, 3 H, CH_3), 8.80 (s, 3 H, CH_3); ^{13}C NMR (C_6D_6) 149.2, 144.4, 140.4, 137.7, 130.0, 128.3, 128.2, 128.1, 127.9, 126.6, 125.9, 125.8, 120.0, 38.4, 36.6, 35.6, 28.7, 24.3, 15.2 ppm; IR (thin film) 3.25, 3.28, 3.31, 3.38, 3.44, 3.51, 6.13, 6.25, 6.69, 6.90, 7.25, 9.24, 9.66, 10.93, 12.20, 13.07, 14.39 μm; UV (95% EtOH) 232 nm (ε 20 961), 270 (1539); MS, m/e 288.1887 (calcd for $C_{22}H_{24}$, m/e 288.1878).

Anal. Calcd for $C_{22}H_{24}$: C, 91.60; H, 8.40. Found: C, 91.40; H, 8.43.

Exploratory Direct Photolysis of *trans*-2,6-Dimethyl-1,6-diphenylspiro[2.5]oct-1-ene. A 250-mL degassed cyclohexane solution of 115 mg (0.40 mmol) of *trans*-2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene was irradiated for 1.0 h (1.60 mEinsteins, 47% conversion) through filter C on the black box apparatus.[36] The solution was concentrated at 25 °C and separated by high-pressure liquid chromatography on a 35 cm X 0.64 cm porous silica microbead[29] column in two 60-mg injections eluted through two recycle modes with 1% methylene chloride in pentane to give the following: 1, 37.9 mg (0.13 mmol, 32.5%) of *cis*-2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene; 2, 56.7 mg (0.20 mmol, 50%) of *trans*-2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene; 3, 9.1 mg (0.03 mmol, 7.5%) of 4-methyl-1-(*cis*-2-methyl-1-phenylethenyl)-4-phenyl-1-cyclohexene.

Exploratory Sensitized Photolysis of *cis*-2,6-Dimethyl-1,6-diphenylspiro[2.5]oct-1-ene. A 250-mL benzene solution of 110 mg (0.38 mmol) of *cis*-2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene and 3.02 g (16.6 mmol) of benzophenone was irradiated for 7.5 h (7.35 mEinsteins, 0% conversion) through filter D on the black box apparatus.[36] The photolysate was concentrated without heat and chromatographed on a 100 cm X 2.0 cm silica gel column eluted with hexane in 500-mL fractions to give the following: 1–3, nil; 4–7, 93.2 mg (0.32 mmol, 85%) of unreacted cyclopropene (some decomposition had occurred); 8, 5% ether in hexane, nil; 9–15, 5% ether in hexane, 2.98 g (16.4 mmol, 98.6%) of benzophenone, mp 47–48 °C.

Exploratory Sensitized Photolysis of *trans*-2,6-Dimethyl-1,6-diphenylspiro[2.5]oct-1-ene. A 250-mL solution of 108 mg (0.38 mmol) of *trans*-2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene and 3.17 g (17.4 mmol) of benzophenone was irradiated for 6.0 h (5.87 mEinsteins, 0% conversion) through filter D on the black box apparatus.[36] The photolysate was concentrated without heat and chromatographed on a 100 cm X 2.0 cm silica gel column eluted with hexane in 500-mL fractions to give the following: 1–3, nil; 4–8, 90.2 mg (0.31 mmol, 83.5%) of unreacted starting cyclopropene (some decomposition had occurred); 9, 5% ether in hexane, nil; 10–18, 5% ether in hexane, 3.08 g (16.9 mmol, 97.2%) of benzophenone, mp 47–48 °C.

1-Hydroxy-4-methyl-1-(*cis*-2-methyl-1-phenylethenyl)-4-phenylcyclohexane. A −78 °C ethereal solution of 2.00 g (10.2 mmol) of *trans*-1-bromo-1-phenylpropene[47] was treated with 6.77 mL of 1.51 M *n*-butyllithium in hexane (0.65 g, 10.2 mmol).[48] The reaction was stirred for 1 h at −78 °C and 15 min at −50 °C before 1.80 g (9.57 mmol) of 4-methyl-4-phenylcyclohexanone in 10 mL of ether was added at −78 °C. The mixture was stirred for 6 h with gradual warming to room temperature and then quenched with ammonium chloride and ether extracted. The organic phase was washed with water and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo to give 4.10 g of a yellow oil. Chromatography on a 50 cm × 2.5 cm silica gel column packed in hexane and eluted in 250-mL fractions gave the following: 1–4, nil; 5–8, 0.25 (2.12 mmol) of *cis*-1-phenylpropene; 9–20, 2.5% ether in hexane, 0.47 g (2.52 mmol) of unreacted 4-methyl-4-phenylcyclohexanone; 21–28, 10% ether in hexane, 1.96 g (6.41 mmol, 62.8%) of 1-hydroxy-4-methyl-1-(*cis*-2-methyl-1-phenylethenyl)-4-phenylcyclohexane as a viscous yellow oil composed of two isomers. The spectral data were as follows: NMR ($CDCl_3$) τ 2.44–3.12 (m, 10 H, arom), 4.05–4.32 (2 q, J = 7.0 Hz, 1 H, vinyl), 7.40–8.98 (complex, 9 H, 4 CH_2, OH), 8.60 and 8.76 (2 d, J = 7.0 Hz, 3 H, CH_3), 8.78 and 8.88 (2 s, 3 H, CH_3); IR (thin film) 2.82, 2.92, 3.27, 3.29, 3.32, 3.40, 3.51, 6.27, 6.37, 6.73, 6.92, 7.27, 9.30, 9.71, 9.95, 10.36, 10.99, 11.83, 13.07, 13.79, 15.90 μm; MS, m/e 306.1977 (calcd for $C_{22}H_{26}O$, m/e 306.1984)

Anal. Calcd for $C_{22}H_{26}O$: C, 86.27; H, 8.56. Found: C, 85.98; H, 8.81.

4-Methyl-1-(*cis*-2-methyl-1-phenylethenyl)-4-phenyl-1-cyclohexene. A mixture of 2.00 mL of glacial acetic acid, 0.20 mL of water, and 0.50 g (1.65 mmol) of 1-hydroxy-4-methyl-1-(*cis*-2-methyl-1-phenylethenyl)-4-phenylcyclohexane at 0 °C was treated with 0.20 mL of concentrated sulfuric acid. The reaction mixture was stirred for 15 min at 0 °C and then added to ice water and ether extracted. The ethereal extract was washed with water, saturated sodium bicarbonate, and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated under vacuum. Purification on a 20 cm × 20 cm thick-layer plate eluted 3 times with hexane afforded one major fast-moving band which proved on workup to be 0.42 g (1.62 mmol, 89.4%) of pure 4-methyl-1-(*cis*-2-methyl-1-phenylethenyl)-4-phenyl-1-cyclohexene identical in every respect (TLC, NMR, ^{13}C NMR, IR, UV, MS, elemental analysis) with the material isolat ed from the photolysate of both *cis*- and *trans*-2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene.

Photolysis Apparatus for Quantum Yield Determinations. All quantum yield determinations were run on the black box apparatus[36] with light output being measured for each run by a digital electronic actinometer[43] calibrated by ferrioxalate actinometry.[44] The band pass was controlled by a filter solution combination held in a 750-mL total volume three-compartment quartz-faced filter solution cell. The filter solution combination employed in the direct runs was as follows: cell 1, 2.00 M nickel sulfate hexahydrate in 10% sulfuric acid; cell 2, 2.00 M cobalt sulfate heptahydrate in 10% sulfuric acid; cell 3, 2.00×10^{-4} M bismuth trichloride in 60% hydrochloric acid; transmission, 0% below 250 nm, 29.5% at 286 nm, 0% above 310 nm (filter C). The filter solution combination used for the sensitized work was as follows: cell 1, 0.19 M nickel sulfate hexahydrate in 10% sulfuric acid; cell 2, 1.00 M, cobalt sulfate heptahydrate in 10% sulfuric acid; cell 3, 0.33 M stannous chloride dihydrate in 60% hydrochloric acid; transmission, 0% below 325 nm, 21.5% at 356 nm, 0% above 390 nm to 530 nm, gradually rising to 4.0% at 580 nm (filter D).

All quantum yield photolyses were run in purified cyclohexane (direct runs) or purified benzene (sensitized runs) purged with

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Table VI. Direct Quantum Yield Photolyses of *cis*- and *trans*-2,6-Dimethyl-1,6-diphenylspiro[2.5]oct-1-ene (3 and 4)[a]

run	% conv	product, mmol	quantum yield	run	% conv	product, mmol	quantum yield
	Series A: Reactant 3, Product 4				Series C: Reactant 4, Product 3		
1	4.00	0.0240	0.24	9	3.93	0.0223	0.24
2	8.98	0.0520	0.20	10	9.61	0.0531	0.19
3	12.4	0.0865	0.19	11	11.1	0.0590	0.14
4	16.9	0.0934	0.15	12	13.6	0.0719	0.13
	Series B: Reactant 3, Product 36				Series D: Reactant 4, Product 36		
5	0.72	0.00392	0.012	13	0.74	0.00420	0.012
6	0.77	0.00417	0.011	14	0.79	0.00444	0.011
7	0.86	0.00458	0.011	15	0.83	0.00465	0.010
8	1.46	0.00466	0.0067	16	1.00	0.00550	0.0089

[a] All runs used 0.5–0.6 mmol of reactant. Series A employed 0.102, 0.256, 0.362, and 0.628 mEinstein of light. Series B used 0.332, 0.380, 0.424, and 0.696 mEinstein. Series C used 0.094, 0.286, 0.425, and 0.559 mEinstein. Series D used 0.362, 0.416, 0.470 and 0.628 mEinstein, respectively.

dry deoxygenated nitrogen for 1 h prior to and during photolysis. The glassware used was base treated to minimize complications due to acid-catalyzed reactions of cyclopropenes.

Direct Quantum Yield Results. All direct runs were analyzed by high-pressure liquid chromatography on a 50 cm × 0.64 cm porous silica microbead[29] column, peaks being integrated with a Summagraphics Bit Pad interfaced with a PDP-11/T55 computer. The internal standard employed was naphthalene. The data are reported in Table VI.

Control Run. Photoreduction of Benzophenone by Benzhydrol. A solution of 2.60 g (14.3 mmol) of benzophenone and 1.11 g (6.04 mmol) of benzhydrol in 750 mL of *tert*-butyl alcohol was irradiated for 7.09 h through filter D on the black box apparatus.[36] The light absorbed was 7.78 mEinsteins. The photolysate was filtered, leaving 351 mg (0.932 mmol) of benzopinacol, mp 193–195 °C. The filtrate was concentrated in vacuo to yield 3.28 g of a clear oil. The residue was chromatographed on a 100 cm × 2.5 cm silica gel column packed in hexane and eluted in 50-mL fractions to give the following: 1–20, 2% ether in hexane, nil; 21–25, 3% ether in hexane, 9.1 mg (0.03 mmol) of benzopinacol, mp 192–193 °C; 26–32, nil; 33–50, 2.16 g (11.9 mmol, 83.0%) of benzophenone, mp 47–49 °C; 51–63, nil; 64–105, 8.5% ether in hexane, 0.99 g (5.38 mmol, 89.1%) of benzhydrol, mp 80–82 °C. The quantum yield of formation of benzopinacol was 0.123.

Energy-Transfer Test. Quenching of Benzophenone Triplets by *cis*-2,6-Dimethyl-1,6-diphenylspiro[2.5]oct-1-ene. A solution of 99.5 mg (0.35 mmol) of *cis*-2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene, 2.51 g (13.8 mmol) of benzophenone, and 1.51 g (8.20 mmol) of benzhydrol in 750 mL of *tert*-butyl alcohol was irradiated for 15.1 h through filter D on the black box apparatus.[36] The light absorbed was 8.16 mEinsteins. The photolysate was concentrated in vacuo to yield 4.18 g of a colorless oil. The oil was chromatographed on a 100 cm × 2.5 cm silica gel column packed in hexane and eluted in 50-mL fractions to give the following: 1–15, 0.75% ether in hexane, nil; 16–24, 91.7 mg (0.318 mmol, 92.1%) of *cis*-2,6-dimethyl-1,6-diphenylspiro-[2.5]oct-1-ene (some decomposition had occurred due to the prolonged irradiation), mp 74–76 °C; 25–30, nil; 31–59, 3% ether in hexane, 2.46 g (13.5 mmol, 98.0%) of benzophenone, mp 47–49 °C; 60–68, nil; 69–180, 7.5% ether in hexane, 1.45 g (7.88 mmol, 96.1%) of benzhydrol, mp 80–81 °C; 181–200, 8.5% ether in hexane, nil. No benzopinacol formation was observed.

Energy-Transfer Test. Quenching of Benzophenone Triplets by *trans*-2,6-Dimethyl-1,6-diphenylspiro[2.5]oct-1-ene. A solution of 101 mg (0.35 mmol) of *trans*-2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene, 2.52 g (13.9 mmol) of benzophenone, and 1.53 g (8.30 mmol) of benzhydrol in 750 mL of *tert*-butyl alcohol was irradiated for 10.1 h through filter D on the black box apparatus.[36] The light absorbed was 8.08 mEinsteins. The photolysate was concentrated in vacuo to yield 4.22 g of a colorless oil. The oil was chromatographed on a 100 cm × 2.5 cm silica gel column packed in hexane and eluted in 50-mL fractions to give the following: 1–17, 0.5% ether in hexane, nil; 18–30, 94.1 mg (0.33 mmol, 93.0%) of *trans*-2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene (some decomposition had occurred due to the prolonged irradiation), mp 75–77 °C; 31–35, nil; 36–61, 3% ether in hexane, 2.48 g (13.6 mmol, 98.4%) of benzophenone, mp 47–49 °C; 62–70, nil; 71–150, 7.5% ether in hexane, 1,49 g (8.10 mmol, 97,5%) of benzhydrol, mp 80–81 °C; 151–160, 8.5% ether in hexane, nil. No benzopinacol formation was observed.

Theromolysis of *cis*-2,6-Dimethyl-1,6-diphenylspiro-[2.5]oct-1-ene. Into a base-washed thick-walled Pyrex tube was placed 76.7 mg (0.27 mmol) of *cis*-2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene. The tube was sealed at 0.05 mm and heated at 150 ± 2 °C for 2.0 h. NMR analysis of the resulting yellow oil showed three compounds to be present—starting cis spirocyclopropene, trans spirocyclopropene, and 4-methyl-1-(*cis*-1-methyl-2-phenylethenyl)-4-phenyl-1-cyclohexene in a ratio of 43:35:22, respectively, relative to *p*-methoxybenzophenone standard. Separation on a 20 cm × 20 cm thick-layer plate eluted 8 times with pentane gave the following: band 1 (R_f 0.58), 57.2 mg (0.20 mmol) of a 1.3:1 mixture of cis/trans spirocyclopropenes; band 2 (R_f 0.54), 14.6 mg (0.05 mmol, 22.1%) of 4-methyl-1-(*cis*-1-methyl-2-phenylethenyl)-4-phenyl-1-cyclohexene. The spectral data for 4-methyl-1-(*cis*-1-methyl-2-phenylethenyl)-4-phenyl-1-cyclohexene were as follows: NMR ($CDCl_3$) τ 2.52–3.05 (m, 10 H, arom), 3.48 (s, 1 H, vinyl), 3.92 (t, J = 2.0 Hz, 1 H, vinyl), 7.11–8.82 (complex, 6 H, 3 CH_2), 8.01 (s, 3 H, CH_3), 8.71 (s, 3 H, CH_3); ^{13}C NMR (C_6D_6) 149.3, 139.2, 137.5, 137.4, 129.6, 128.4, 128.2, 127.9, 127.4, 126.2, 125.9, 124.9, 123.7, 38.7, 36.2, 35.5, 28.5, 24.1, 15.3 ppm; IR (thin film) 3.27, 3.30, 3.33, 3.40, 3.45, 3.53, 6.27, 6.33, 6.73, 6.94, 7.29, 9.30, 9.71, 10.87, 12.42, 13.16, 13.99, 14.39 μm; UV (95% EtOH) 252 nm (ϵ 12 355), 265 (14 414); MS, m/e 288.1874 (calcd for $C_{22}H_{24}$, m/e 288.1878).

Anal. Calcd for $C_{22}H_{24}$: C, 91.60; H, 8.40. Found: C, 91.47; H, 8.36.

Thermolysis of *trans*-2,6-Dimethyl-1,6-diphenylspiro-[2.5]oct-1-ene. A base-washed thick-walled Pyrex tube was charged with 55.0 mg (0.19 mmol) of *trans*-2,6-dimethyl-1,6-diphenylspiro[2.5]oct-1-ene, the tube sealed under 0.05 mm and heated at 150 ± 2 °C for 2.0 h. NMR of the resulting yellow oil indicated the presence of three compounds—starting trans spirocyclopropene, cis spirocyclopropene, and 4-methyl-1-(*cis*-2-methyl-1-phenylethenyl)-4-phenyl-1-cyclohexene in a ratio of 54:33:13, respectively, relative to *p*-methoxybenzophenone standard. Chromatography on a 20 cm × 20 cm thick-layer plate eluted 6 times with hexane gave the following: band 1 (R_f 0.67), 46.3 mg (0.16 mmol) of a 1.3:1 mixture of trans/cis spirocyclopropenes; band 2 (R_f 0.60), 7.8 mg (0.03 mmol, 14.2%) of 4-methyl-1-(*cis*-2-methyl-1-phenylethenyl)-4-phenyl-1-cyclohexene identical in every respect (TLC, NMR, ^{13}C NMR, IR, UV, MS, elemental analysis) with the material isolated from the photolyses of the cis and trans spirocyclopropenes.

Spirocyclopropene Thermal Chemistry Results. All thermolyses were performed in base-washed thick-walled Pyrex tubes sealed under 0.05-mm vacuum. The products were separated by high-pressure liquid chromatography on a 50 cm × 0.64 cm porous silica microbead[29] column (50-mg injections, three recycle modes) and analyzed spectrally. Stereoisomer **3** (0.270 mmol) was thermolyzed at 150 °C for 2 h to 50% conversion to afford 41.4 % (0.112 mmol) of **3**, 32.0 % (0.086 mmol) of **4**, and 21.1 % (0.051 mmol) of **37**. Parallel thermolysis of **4** (0.190 mmol) for 2.30 h gave 46% conversion to afford 33.8% (0.064 mmol) of

3, 50.8% (0.097 mmol) of 4, and 14.2% (0.027 mmol) of 36.

***trans*-2-Bromo-1-phenylpropene.** By use of the method of Grovenstein and Lee,[49] 10.0 g (31.0 mmol) of 2,3-dibromo-2-methyl-3-phenylpropionic acid was reacted to give 4.02 g (20.4 mmol, 65.8%) of *trans*-2-bromo-1-phenylpropene. Purification was effected by rapidly passing the neat compound through a 5 cm × 0.5 cm alumina column to give 3.58 g (18.2 mmol, 58.6%) of the pure vinyl bromide.

1-Hydroxy-4-methyl-1-(*cis*-1-methyl-2-phenylethenyl)-4-phenylcyclohexane. A −100 °C solution of 1.00 g (5.08 mmol) of *trans*-2-bromo-1-phenylpropene was treated with 3.72 mL of a 1.40 M pentane solution of *tert*-butyllithium (0.33 g, 5.20 mmol).[48] The reaction was stirred for 2 h at −100 °C before a 10-mL ether solution of 0.90 g (4.80 mmol) of 4-methyl-4-phenylcyclohexanone was introduced dropwise. Stirring was continued for 6 h with gradual warming to ambient temperature and then quenched with ammonium chloride and ether extracted. The combined extract was washed with water and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo to give 2.30 g of a yellow oil. Chromatography on a 50 cm × 1.5 cm silica gel column packed in hexane and eluted in 250-mL fractions then gave the following: 1–4, nil; 5–8, 0.09 g (0.76 mmol) of *cis*-1-phenylpropene; 9–12, 2.5% ether in hexane, 0.21 g (1.11 mmol) of unreacted 4-methyl-4-phenylcyclohexanone; 13–18, 10% ether in hexane, 0.87 g (2.51 mmol, 51.4%) of 1-hydroxy-4-methyl-1-(*cis*-1-methyl-2-phenylethenyl)-4-phenylcyclohexane as a viscous yellow oil composed of two isomers. The spectral data were as follows: NMR ($CDCl_3$) τ 2.40–3.03 (m, 10 H, arom), 3.56 and 3.68 (2 s, 1 H, vinyl), 7.27–8.98 (complex, 8 H, 4 CH_2), 7.66 (s, 3 H, CH_3), 8.67 and 8.73 (2 s, 3 H, CH_3); IR (thin film) 2.81, 2.91, 3.27, 3.29, 3.33, 3.42, 3.52, 6.27, 6.71, 6.87, 6.94, 7.27, 7.91, 8.26, 8.44, 9.30, 9.71, 10.00, 10.42, 10.92, 13.16, 14.29 μm; MS, m/e 306.1986 (calcd for $C_{22}H_{26}O$, m/e 306.1984).

Anal. Calcd for $C_{22}H_{26}O$: C, 86.27; H, 8.56. Found: C, 85.85; H, 8.83.

4-Methyl-1-(*cis*-1-methyl-2-phenylethenyl)-4-phenyl-1-cyclohexene. By a procedure identical with that for the preparation of 4-methyl-1-(*cis*-2-methyl-1-phenylethenyl)-4-phenyl-1-cyclohexene, 0.50 g (1.63 mmol) of 1-hydroxy-4-methyl-1-(*cis*-1-methyl-2-phenylethenyl)-4-phenylcyclohexane was reacted to give 0.49 g of crude olefin. Purification on a 20 cm × 20 cm thick-layer plate gave one band which proved on workup to be 0.40 g (1.39 mmol, 85.3%) of pure 4-methyl-1-(*cis*-1-methyl-2-phenylethenyl)-4-phenyl-1-cyclohexene identical in every respect (TLC, NMR, ^{13}C NMR, IR, UV, MS, elemental analysis) with the material isolated in the thermolysis of the trans spirocyclopropene.

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Registry No. **1**, 82323-13-5; **2**, 82323-14-6; **3**, 82323-15-7; **4**, 82323-16-8; **5**, 82323-17-9; **7**, 82323-18-0; **9**, 82323-19-1; **10**, 82323-20-4; **11**, 82323-21-5; **12**, 82323-22-6; **14**, 82323-23-7; **16**, 18932-33-7; **17**, 82323-24-8; **18**, 82323-25-9; **19**, 82323-26-0; **20**, 82323-27-1; **21**, 82323-28-2; **23**, 82323-29-3; **24**, 82323-30-6; **25**, 82323-31-7; **26**, 82323-32-8; **27**, 82323-33-9; **28**, 82323-34-0; **30**, 57132-29-3; **31**, 82323-35-1; **32**, 82323-36-2; **33**, 82323-37-3; **34**, 82323-38-4; **35**, 82337-92-6; **36**, 82337-93-7; **37**, 82337-94-8; **38**, 82337-95-9; **39**, 82337-96-0; **47**, 82323-39-5; *trans*-2-methyl-1,3-diphenyl-2-propen-1-one tosylhydrazone, 82323-40-8; 2-methyl-1,3-diphenylcyclopropene, 65102-39-8; 3-methyl-1,2-diphenylcyclopropenyl BF_4^-, 65102-02-5; 3-hydroxy-2-phenylpropene, 6006-81-1; 1-bromo-1-phenylethene, 98-81-7; formaldehyde, 50-00-0; 3-chloro-2-phenylpropene, 3360-52-9; *p*-(dimethylamino)benzophenone, 530-44-9; 2,3,5-triphenyltoluene, 82323-41-9; 1-phenyl-2-butanone, 1007-32-5; 1,2-diphenyl-2-propen-1-one, 4452-11-3; 2-methyl-3,4,6-triphenyl-2-cyclohexen-1-one, 82323-42-0; 2-methyl-3,4,6-triphenyl-2-cyclohexen-1-ol, 82323-43-1; 3-methyl-1,4,5-triphenyl-1,3-cyclohexadiene, 82323-44-2; 4-phenyl-3-penten-2-one, 827-69-0; deoxybenzoin, 451-40-1; 2-oxophenylacetic acid, 611-73-4; *p*-toluenesulfonohydrazide, 1576-35-8; 2-oxophenylacetic acid tosylhydrazone, 82323-45-3; 2-oxophenylacetyl chloride tosylhydrazone, 82323-46-4; acetaldehyde, 75-07-0; 1,3-diphenyl-2-propanone, 102-04-5; methyl vinyl ketone, 78-94-4; 3-methyl-1,2,6-triphenyl-2-cyclohexen-1-ol, 82323-47-5; 1-phenyl-2-propen-1-one, 768-03-6; 2-methyl-1,3,6-triphenyl-2-cyclohexen-1-ol, 82323-48-6; benzyltriphenylphosphonium chloride, 1100-88-5; 1-benzylidene-4-methyl-4-phenylcyclohexane, 82323-49-7; 1-bromo-1-(1-bromobenzyl)-4-methyl-4-phenylcyclohexane, 82323-50-0; 1-(1-bromobenzylidene)-4-methyl-4-phenylcyclohexane, 82323-51-1; 1-(4-methyl-4-phenylcyclohexylidene)-1-phenyl-2-propanone, 82323-52-2; *trans*-1-bromo-1-phenylpropene, 31076-47-8; *cis*-1-bromo-1-phenylpropene, 31026-78-5; benzophenone, 119-61-9; benzhydrol, 91-01-0.