Cyclopropanols and the Di-π-methane Rearrangement: Mechanistic and Exploratory Organic Photochemistry[1,2]

Howard E. Zimmerman,* John M. Nuss, and Anthony W. Tantillo

Chemistry Department, University of Wisconsin, Madison, Wisconsin 53706

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The photochemistry of a series of di-π-methane systems, having a hydroxyl group on the methane carbon, was investigated. Both the divinyl and the aryl vinyl versions were studied. In certain cases, an isomeric γ,δ-unsaturated ketone was obtained; the reactant a-b-c-d-e carbon skeletal sequence was permuted to afford the product with the sequence c-a-b-d-e. In two cases intermediate cyclopropanols could be isolated and in all instances evidence was obtained that the bizarre rearrangement resulted from a di-π-methane rearrangement followed by ring opening of the resultant cyclopropanol. Photolysis of the corresponding phenyldimethylsilyl ethers led nicely to the corresponding cyclopropyl ethers in all cases. Tetrabutylammonium fluoride treatment resulted in ring opening. Quantum yields and reaction multiplicites were determined. Direct and sensitized irradiations established both singlet and triplet reactivity. The photochemistry of the cyclopropane products revealed cis–trans isomerization of the silyl ethers and, additionally, ring opening of the cyclopropanols. One of the reactions proved reversible, thus 1,2,2,5,5-pentaphenylpent-4-en-1-one afforded the stereoisomeric 1,2,2-triphenyl-3-[2,2-diphenylvinyl]cyclopropanols. Single photon counting was employed to obtain the excited singlet lifetime and reaction rate for 1,1,3,3-tetraphenyl-2-propen-1-ol.

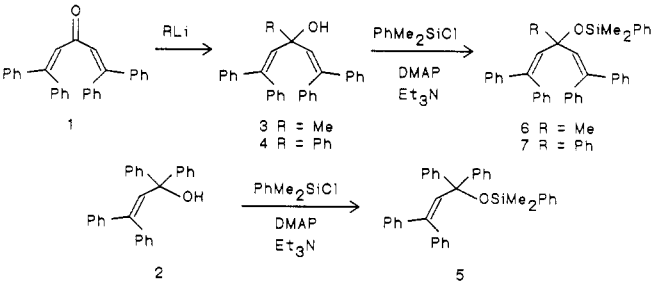
Introduction

Over two decades ago we described the di-π-methane rearrangement, its generality and basic mechanism.[3a-d] In the intervening period we pursued studies investigating the stereochemistry,[3e-h] regioselectivity,[3i-k] substituent effects,[3j,k] multiplicity,[3c,g,l,m] structural requirements,[3n,o] and other features[4] of the reaction. Despite this extensive series of investigations, we have maintained an interest in searching for novel variations as well as exploring subtleties of the reaction. With this in mind, we proceeded to study the di-π-methane rearrangement of molecules having central hydroxy substitution.

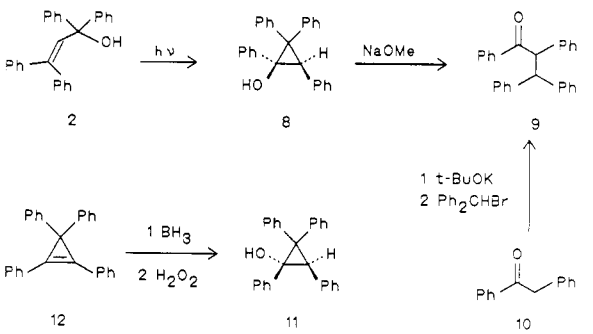
Results

Synthesis of Photochemical Reactants. We synthesized 1,1,5,5-tetraphenyl-3-methyl-1,4-pentadien-3-ol (**3**), 1,1,3,5,5-pentaphenyl-1,4-pentadien-3-ol (**4**), and 1,1,3,3-tetraphenyl-2-propen-1-ol (**2**).[5] In addition, we prepared the corresponding phenyldimethylsilyl ethers **5**, **6** and **7**, respectively. Our syntheses of these compounds are outlined in Scheme I.

Scheme I. Synthesis of Photochemical Reactants, Products, and Related Compounds



Scheme II. Photolysis of the Tetraphenylpropenol 2 and Structure Proof of the Photoproduct 8



Exploratory Photolysis of the Tetraphenylpropenol and Its Phenyldimethylsilyl Ether. Exploratory irradiation of the tetraphenylpropenol **2** led to a single, crystalline photoproduct, mp 121–124 °C. The NMR spectrum revealed a single aliphatic methine singlet at δ 3.64 in addition to absorption corresponding to 20 aromatic hydrogens. An additional peak at δ 2.28 was ascribed to a hydroxyl hydrogen, and this was confirmed by the infrared spectrum which had a non-hydrogen-bonded hydroxyl absorption at 3580 cm^{-1}. The tentative structural assignment of 1,2,2,3-tetraphenylcyclopropanol (**8**) to the 124 °C photoproduct was confirmed by its conversion, on mild methoxide treatment, to 1,2,3,3-tetraphenyl-1-propanone (**9**), which was independently synthesized. Note Scheme II for the degradation to **9** and the synthesis of

(1) This is Paper 153 of our photochemical series and Paper 213 of the general series.

(2) For Paper 152 see: Zimmerman, H. E.; Carpenter, C. W. *J. Org. Chem.* **1988**, *53*, 3298-3305.

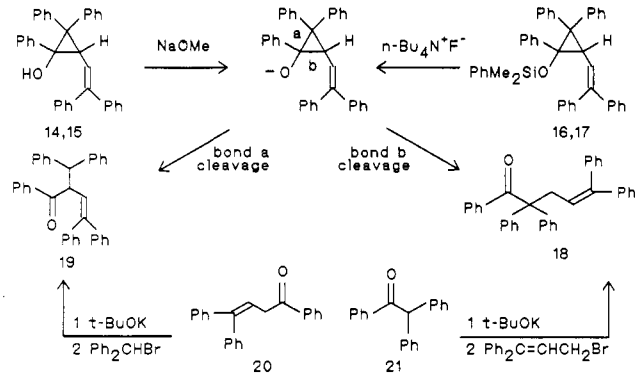
(3) (a) One early example was that of the barrelene to semibullvalene rearrangement: Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183-184. (b) The mechanism was proposed by: Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932-3933. (c) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718-1727. (d) Zimmerman, H. E.; Givens, R. S.; Pagni, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 4191-4193. (e) Zimmerman, H. E.; Gannett, T. P.; Keck, G. E. *J. Org. Chem.* **1979**, *44*, 1982-1989. (f) Zimmerman, H. E.; Robbins, J. D.; McKelvey, R. D.; Samuel, C. J.; Sousa, L. R. *J. Am. Chem. Soc.* **1974**, *96*, 4630-4643. (g) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 6267-6272. (h) Zimmerman, H. E.; Baeckstrom, P.; Johnson, T.; Kurtz, D. W. *J. Am. Chem. Soc.* **1974**, *96*, 1459-1465. (i) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 6259-6267. (j) Zimmerman, H. E.; Welter, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 4131-4145. (k) Zimmerman, H. E.; Cotter, B. R. *J. Am. Chem. Soc.* **1974**, *96*, 7445-7453. (l) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1975**, *97*, 3718-3725. (m) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 8749-8761. (n) Zimmerman, H. E.; Pincock, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 2957-2963. (o) Zimmerman, H. E.; Little, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 5143-5152.

(4) (a) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531-551. (b) Zimmerman, H. E.; Döpp, D. *Methods of Organic Chemistry (Houber-Weyl)*; G. Thieme Verlag: Stuttgart, 1975; pp 413-448. (c) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; DeMayo, P., Ed.; Academic: New York, 1980; Vol. 3.

(5) Ubelholde, A. R.; Burgess, J. *J. Chem. Soc. B* **1970**, 1106-1113.

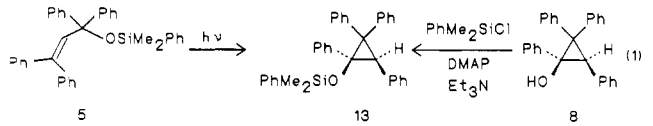
0022-3263/88/1953-3792$01.50/0

Scheme III. Ring-Opening Reactions of Photoproducts



this compound as well as the photochemistry affording tetraphenylcyclopropanol **8**. The stereochemistry of photoproduct **8** was established by synthesis of the corresponding stereoisomer **11** whose configuration is assigned on the basis that hydroboration should be syn.[6]

Also, the corresponding phenyldimethylsilyl ether **5** of tetraphenylpropenol **2** was irradiated and afforded a single photoproduct **13**. This exhibited an NMR spectrum quite similar to that of tetraphenylcyclopropanol **8** except for additional absorption (cf. the Experimental Section) due to the phenyldimethylsilyl moiety. The structural assignment was confirmed by its formation from the tetraphenyl cyclopropanol **8** by phenyldimethyl silylation. The photochemistry and structure proof are outlined in eq 1.



We note that the reaction is again stereoselective and favors the stereoisomer having trans phenyl groups. Interestingly, sensitized irradiation of the tetraphenylpropenol **2** led to no reaction.

Exploratory Photochemistry of Pentaphenylpentadienol 4. Direct irradiation of pentaphenylpentadienol **4** led to two photoproducts, **14** and **15**. Similar irradiation of the corresponding pentaphenyl silyl ether **7** afforded two related photoproducts, **16** and **17**.

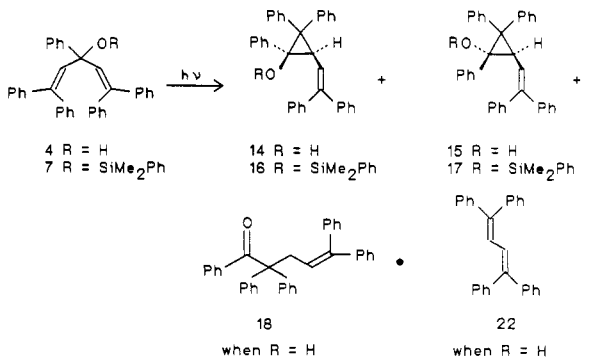
The NMR spectra of the two photoproducts **14** and **15**, obtained on irradiation of pentaphenylpentadienol **4**, showed methine and vinyl peaks, suggesting that these were vinyl cyclopropanol stereoisomers. The NMR spectra of the silyl ether photoproducts **16** and **17** were quite similar and suggested that these were the corresponding phenyldimethylsilyl ethers of photoproducts **14** and **15**.

It was found that treatment of each of the cyclopropanol photoproducts (i.e., **14** and **15**) with sodium methoxide in methanol led to two ketonic products, **18** and **19**. Treatment of each of the silyl ether photoproducts (i.e., **16** and **17**) with tetrabutylammonium fluoride in tetrahydrofuran afforded the same two ketonic degradation products. We interpreted these degradations as ring openings of cyclopropanols and silyl derivatives as depicted in Scheme III. The structure, including stereochemistry, of the cis pentaphenyl cyclopropyl silyl ether **16** was established by X-ray diffraction. Details are given in the supplementary material.

In addition to the primary photoproducts there were two secondary photoproducts, **18** and **22**, in the irradiations of the pentaphenyl dienol **4**. Hence, the direct photochemistry of the pentaphenyl compounds may be written

(6) Brown, H. C.; Rhodes, S. P. *J. Am. Chem. Soc.* **1969**, *91*, 4306–4307.

Scheme IV. Photochemistry of Pentaphenyl Dienol 4 and Its Phenyldimethyl Silyl Ether



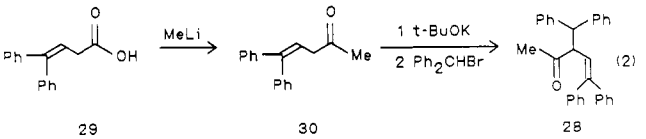
as in Scheme IV. A control run in the dark demonstrated that pentaphenyl cyclopropanols **14** and **15** were thermally stable and had proceeded onward to pentaphenyl ketone **18** only photochemically.

Interestingly, sensitization of the pentaphenyl pentadienol **4** with (dimethylamino)benzophenone (E_T 65 kcal/mol)[7] under conditions where only the sensitizer absorbed light led to the same reaction (i.e., formation of **14** and **15**) as observed on direct irradiation. While efficient energy transfer to the diphenylvinyl moiety (E_T 59 kcal/mol)[8] is anticipated, the triplet reactivity was in contrast to most diphenylvinyl containing reactants, for example the other hydroxy diphenylvinyl reactants of this study. This point is discussed below. Similarly, the corresponding silyl ether **7** on sensitization gave the same cyclopropane products **16** and **17** as in the direct runs. Nevertheless, variations in the ratios obtained were observed.

Exploratory Photochemistry of Tetraphenylpentadienol 3. This reactant afforded three major photoproducts on direct irradiation in runs utilizing NMR monitoring. Two of these products, **23** and **24**, were hydroxylic and the third, **25**, was a ketone. Attempted HPLC separation led to loss of the hydroxylic products; however, workup with phenyldimethylsilylation was successful and afforded the corresponding phenyldimethylsilyl ethers **26** and **27**.

The structural assignment of these silyl ethers as cis and trans stereoisomers of the (silyloxy)cyclopropanes **26** and **27** was suggested by their NMR spectra, which exhibited methyl singlets at δ 1.28 and 1.58, respectively, and AB quartets (δ 2.23 and 5.67, J = 10.4 Hz for **26**; δ 2.62 and 5.53, J = 10.8 Hz for **27**).

Treatment of the two silyl ethers **26** and **27** with tetrabutylammonium fluoride afforded, in each case, the same two ketones **25** and **28**. The former had been observed from the photochemistry of the tetraphenyl dienol **3**. Ketone **25** proved to be the known[9] 3,3,6,6-tetraphenyl-5-hexen-2-one, and ketone **28** was synthesized independently as outlined in eq 2.



(7) (a) This value is taken from data found in ref 7b and 7c; note ref 7d and 7e; (b) Porter, G.; Suppan, P. *Trans. Faraday Soc.* **1965**, *61*, 1664–1673. (c) O'Connell, E. J., Jr. *J. Chem. Soc., Chem. Commun.* **1969**, 517–572; (d) Zimmerman, H. E.; Ramsden, W. D. *Can. J. Chem.* **1984**, *62*, 2592–2611. (e) Zimmerman, H. E.; Fleming, S. A. *J. Org. Chem.* **1985**, *50*, 2539–2551.

(8) Görner, H. *J. Phys. Chem.* **1982**, *86*, 2028–2035.

(9) Zimmerman, H. E.; Oaks, F. L., to be published.

Table I. Quantum Yield Determinations[a,b]

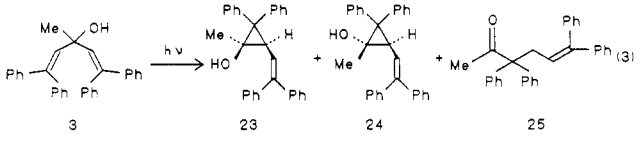
reactant	additive	cyclopropane cis	cyclopropane trans
2[a]	none	0.0071 ± 0.0007 (8)	
2[b]	none	0.024 ± 0.003 (8)	
2[a]	acetophenone	<0.0001	<0.0001
3[b]	none	0.20 ± 0.02 (23)	0.19 ± 0.02 (24)
3[b]	xanthone	<0.025 (23)	<0.025 (24)
4[b]	none	0.24 ± 0.02 (14)	0.067 ± 0.007 (15)
4[b]	xanthone	0.47 ± 0.05 (14)	0.049 ± 0.005 (15)
6[b]	none	0.22 ± 0.02 (26)	0.34 ± 0.03 (27)
6[b]	xanthone	<0.02 (26)	<0.02 (27)
7[b]	none	0.16 ± 0.016 (16)	0.12 ± 0.01 (17)
7[b]	xanthone	0.49 ± 0.04 (16)	0.090 ± 0.009 (17)
18[b]	none	0.0040 ± 0.0007 (14)	0.0044 ± 0.0009 (15)

[a] Solvent *tert*-butyl alcohol. [b] Solvent acetonitrile.

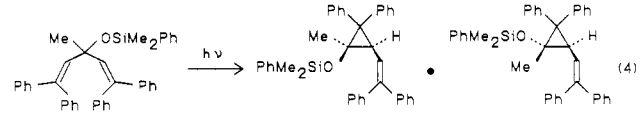
The stereochemical assignments of the tetraphenyl silyl ethers **26** and **27** derive from NOE experiments which revealed a 13.5% enhancement of the cyclopropyl methine for stereoisomer **26** when the methyl group was irradiated compared with no enhancement for stereoisomer **27**, thereby providing evidence for proximity of the methine and methyl groups in **26**. In agreement with this conclusion, there was observed a 15.7% increase in the vinyl peak in compound **27** on irradiation of the methyl group, showing proximity of the vinyl and methyl groups in this stereoisomer.

Interestingly, when the photolysis of tetraphenylpentadienol **3** was interrupted and the mixture monitored in the dark by NMR, no thermal conversion of the tetraphenyl cyclopropanols to tetraphenyl ketone **25** could be detected. However, photolysis did lead onward to this ketone, thus demonstrating that cyclopropanol ring opening results from secondary photochemistry.

Thus, the photochemistry of tetraphenylpentadienol **3** and its silyl ether **6** may be depicted as in eq 3 and 4.



3 23 24 25 (3)

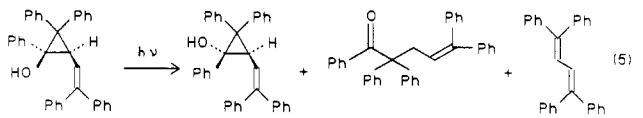


6 26 27 (4)

Quantum Yield Determinations of the Photorearrangements Affording Cyclopropanols and Cyclopropanol Ethers. Quantum yields were determined by using the black box apparatus, described by us earlier,[10] for the direct irradiations and the microbench apparatus[10] for sensitized runs. The previously described[11] electronic actinometer was employed along with ferrioxalate[12] calibration. Product determination by HPLC did not prove feasible due to ring opening of the cyclopropanols during separation. Assays were therefore made by using NMR with sufficient scans to ensure reproducibility, and synthetic mixtures were utilized to estimate experimental error. The quantum yield determinations are summarized in Table I.

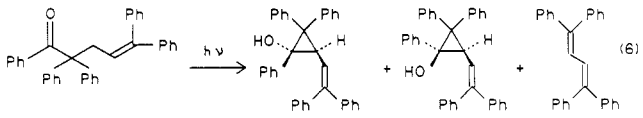
It can be seen that only pentaphenyl dienol **4** and the corresponding silyl ether **7** have reactive triplets. This point is considered subsequently.

Photochemistry of the Pentaphenyl Cyclopropanes. Direct irradiation of the cis isomer of pentaphenyl cyclopropanol **14** afforded the trans stereoisomer **15** along with the pentaphenyl ketone **18** and tetraphenylbutadiene **22**. The same products were obtained in runs with (dimethylamino)benzophenone sensitization (see eq 5). The corresponding silyl ethers were stereoisomerized on direct and sensitized irradiations, but no ring-opening products were encountered.



14 15 18 22 (5)

An Unusual Reversion of the Pentaphenyl Ketone 18 To Afford the Pentaphenyl Cyclopropanols 14 and 15. Remarkably, the irradiation of pentaphenyl ketone **18** afforded the stereoisomeric cyclopropanols, thus revealing that the ring-opening reaction, described above, is reversible. In addition, tetraphenylbutadiene **22** was formed as a minor product. This photochemistry is described in eq 6.



18 15 14 22 (6)

Determination of Excited Singlet Rate Constants for the Tetraphenylpropenol 2. It was of interest to determine the rate of S_1 decay and reaction, since comparable rate constants are known for a number of nonhydroxylic di-π-methane reactants.[3j,13]

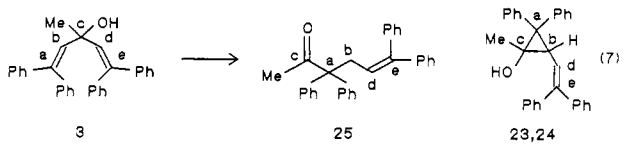
To obtain the rate of excited state decay (i.e., the $k_{d(tot)}$) we used the single photon counting technique we have employed in previous studies.[13a,14] A lifetime of 2.6 ns was obtained at 77 K, while that at room temperature was only marginally measurable. Therefore the method of magic multipliers[13a] was employed, using the ratio of low to room temperature fluorescence intensities. This gives 35 as the ratio of low-temperature to room-temperature lifetimes. This led to 74 ps as the room temperature (i.e., 22 °C) lifetime, corresponding to a total rate of excited singlet decay (i.e., $k_{d(tot)}$) of 1.33×10^{10} s^{-1}. Knowing the reaction quantum yield as $\phi = 0.0071$, we obtain from the relationship $k_r = \phi k_{d(tot)}$ a value of 9.31×10^7 for k_r. The significance of these results is discussed below. Single photon counting measurements on dienes **3**, **4**, and **7** were unsuccessful due to emission not characteristic of the diphenylvinyl moiety despite rigorous purification.

Interpretative Discussion

The Overall Course of the Photochemistry of the Hydroxy Di-π-methane Systems. One of the most remarkable results is the skeletal transformation observed

(10) Zimmerman, H. E. *Mol. Photochem.* **1971**, *3*, 281–292.
(11) Zimmerman, H. E.; Cutler, T. P.; Fitzgerald, V. R.; Weight, T. J. *Mol. Photochemistry* **1977**, *8*, 379–385.
(12) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518–536.
(13) (a) Zimmerman, H. E.; Werthemann, D. P.; Kamm, K. S. *J. Am. Chem. Soc.* **1974**, *96*, 439–449. (b) Zimmerman, H. E.; Steinmetz, M. G.; Kreil, C. L. *J. Am. Chem. Soc.* **1978**, *100*, 4146–4162. (c) Zimmerman, H. E.; Armesto, D.; Amezua, M. G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367–6383.
(14) Zimmerman, H. E.; Cutler, T. P. *J. Chem. Soc., Chem. Commun.* **1975**, 598–599. Zimmerman, H. E.; Penn, J. H.; Carpenter, C. W. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 2128–2132.

in the hydroxy di-π-methane rearrangement plus cyclopropanol-opening reaction. For the case of the formation of the tetraphenyl ketone **25** from tetraphenyl dienol **3**, inspection of eq 7 reveals that an initial skeletal sequence of carbons a-b-c-d-e is converted to the sequence c-a-b-d-e. However, the result is readily understandable in terms of the proposed reaction mechanism (vide infra).



3 25 23,24

It is clear that the primary photoproducts are the cyclopropanes resulting from the di-π-methane rearrangement. Although the cyclopropanols are sensitive to thermal and photochemical ring opening to ketonic products, in the cases of tetraphenylpropenol **2** and pentaphenyl dienol **4**, it was possible to obtain these cyclopropanols without appreciable ring opening.

Consequently, the di-π-methane rearrangement of the silyl ethers is the more practical route to the cyclopropyl products, since the (silyloxy)cyclopropanes are stable photochemically.

Reaction Multiplicity. It has been noted that with sensitization,[15] the tetraphenylpropenol the tetraphenyl dienol **3**, and the tetraphenyl silyl ether **6** were all very slow to form product. We conclude that these have unreactive triplets.

In contrast, the pentaphenyl dienol **4** and its corresponding silyl ether **7** did undergo di-π-methane rearrangements on sensitization, as may be seen in Table I. This has analogy in our previous studies where phenyl substitution on the methane carbon provides reactive triplets.[13c,17]

Ordinarily, when one observes product formation both in direct and sensitized runs, this merely demonstrates that the triplet is capable of reaction. The result, however, does not indicate whether in the direct photolysis it is the singlet reacting or, instead, intersystem crossing to a reactive triplet is occurring.

In the present instance, use is made of a bracketing treatment we described in earlier work.[18] In its simplest form, in eq 8, the direct quantum efficiency is seen to set

$$\phi^{DIR} - \phi^{SENS} \leq {}^1\phi \leq \phi^{DIR} \quad (8)$$

an upper limit on the singlet efficiency while the difference $(\phi^{DIR} - \phi^{SENS})$ provides a lower limit. The limits obtained are listed in Table II.

Table II. Limits Set by Bracketing Relationships

Results from Equation 8: Limits on the Direct Quantum Yield	
pentaphenyl dienol **4**	
photolysis	
$0 \leq {}^1\phi \leq 0.24$	derived from cis quantum yields
$0.018 \leq {}^1\phi \leq 0.067$	derived from trans quantum yields
pentaphenyl silyl ether **7**	
photolysis	
$0 \leq {}^1\phi \leq 0.16$	derived from cis quantum yields
$0.030 \leq {}^1\phi \leq 0.12$	derived from trans quantum yields
Results from Equation 9: Limits on the ISC Efficiency	
pentaphenyl dienol **4**	
photolysis	
$0 \leq \phi_{ISC} \leq 0.53$	with cis cyclopropanol taken as B[a]
$0 \leq \phi_{ISC} \leq 1.37$	with trans cyclopropanol taken as B[b]
pentaphenyl silyl ether **7**	
photolysis	
$0 \leq \phi_{ISC} \leq 0.33$	with cis silyl ether taken as B[a]
$0 \leq \phi_{ISC} \leq 1.33$	with trans silyl ether taken as B[b]
Results from Equation 10	
pentaphenyl dienol **4**	
photolysis	
$0.0 \leq {}^1\phi \leq 0.24$	derived from cis quantum yields
$0.042 \leq {}^1\phi \leq 0.067$	derived from trans quantum yields
pentaphenyl silyl ether **7**	
photolysis	
$0.0 \leq {}^1\phi\ 0.16$	derived from cis quantum yields
$0.091 \leq {}^1\phi \leq 0.12$	derived from trans quantum yields

[a] More stringent limit, thus used. [b] Less stringent limit, not used.

Also, limits on the intersystem crossing efficiency may be determined by using eq 9. If we assign cis as B, we

$$0 \leq \phi_{ISC} \leq (\phi_B{}^{DIR})/(\phi_B{}^{SENS}) \quad (9)$$

obtain an upper limit of 0.53, while if we assume trans to be B, the upper limit becomes 1.37 as given in Table II. With either assignment to B, the lower limit is given as zero by eq 9. The useful limit results from designating B as the cis isomer which then gives ϕ_{ISC} below 0.53.

The same treatment may be applied to the photolysis of the pentaphenyl silyl ether **7** (refer to Table II), where an upper limit of 0.33 results for ϕ_{ISC}.

Still more useful limits on the singlet efficiencies are possible,[18b] in cases such as the present ones, where two photoproducts result from one reaction. Here we utilize eq 10 and select as B the product for which eq 9 gives the more stringent limit for ϕ_{ISC}. Thus B is assigned as the

$$\phi_A{}^{DIR} - ({}^3\phi_A)(\phi_B{}^{DIR})/({}^3\phi_B) \leq {}^1\phi_A \leq \phi_A{}^{DIR} \quad (10)$$

cis isomer and A as the trans. As seen in Table II, this leads to limits for formation of the trans cyclopropanol from the singlet as $0.042 \leq {}^1\phi \leq 0.067$ and for formation of the trans silyl ether as $0.091 \leq {}^1\phi \leq 0.12$. The limits for the cis isomers are $0 \leq {}^1\phi \leq 0.24$ for the cyclopropanol and $0 \leq {}^1\phi \leq 0.16$ for the silyl ether and not useful.

An interesting comparison is the estimate by Görner,[8] giving an upper limit of 0.001 for the intersystem crossing efficiency of 1,1-diphenylethylene. Thus, our upper limits of 0.53 and 0.33 for intersystem crossing of the pentaphenyl dienol **4** and the pentaphenyl silyl ether **7** may be due to enhancement of intersystem crossing of the diphenylvinyl moiety present in both or may just be very high upper limits.

If our intersystem crossing efficiencies are actually zero, then all of the direct irradiations would be proceeding via the singlet excited state and only the sensitized runs would be using the triplet excited state.

Aspects of the Di-π-methane Rearrangement Mechanism. The di-π-methane rearrangement mechanism applied to the hydroxy and silyloxy systems studied

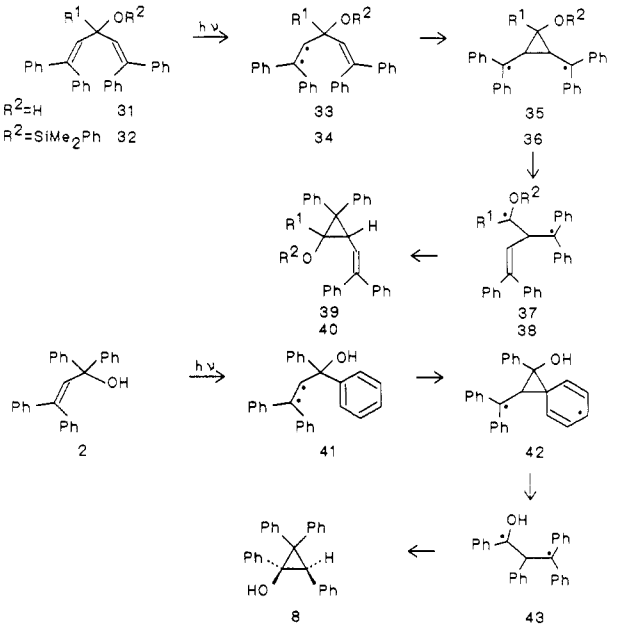
(15) In each case, the reactant concentration was maintained at ca. 2×10^{-3} M, a concentration where the rate of energy transfer is much greater than the rate of sensitizer triplet decay. Thus we assume that energy transfer will be diffusion controlled in view of the exothermicity of triplet transfer from xanthone (E_T 74 kcal/mol)[16a] and acetophenone (E_T 74 kcal/mol)[16b] to molecules with a diphenylvinyl moiety (E_T 59 kcal/mol).[7] These rates (1.1×10^{10} L M^{-1} s^{-1} in acetonitrile[16c] and 6.7×10^9 L M^{-1} s^{-1} in *tert*-butyl alcohol[16d]) multiplied by the substrate concentration (maintained near 2×10^{-3} M) are large compared with the rates of decay of the xanthone (^3k_d 2×10^4 s^{-1} [16a]) and acetophenone (2×10^6 s^{-1} [16e]).

(16) (a) Pownall, H. J.; Huber, J. R. *J. Am. Chem. Soc.* **1973**, *93*, 6429–6436. (b) Yang, N. C.; McClure, D. S.; Murov, S. L.; Houser, J. J.; Dusenbery, R. L. *J. Am. Chem. Soc.* **1967**, *89*, 5466–5468. (c) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898–5901. (d) Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232–2238. (e) Yang, N. C.; Dusenbery, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 5899–5900.

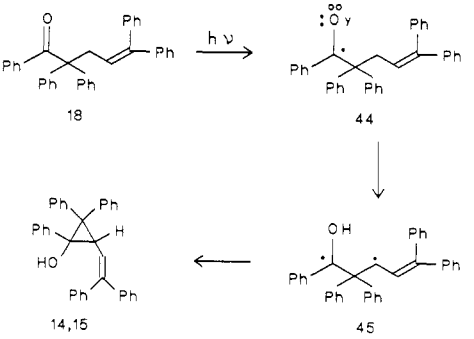
(17) (a) Zimmerman, H. E.; Boettcher, R. J.; Braig, W. *J. Am. Chem. Soc.* **1973**, *95*, 2155–2163. (b) Zimmerman, H. E.; Factor, R. E. *Tetrahedron, Suppl. 1* **1981**, *37*, 125–141.

(18) (a) Zimmerman, H. E.; Kreil, D. J. *J. Org. Chem.* **1982**, *47*, 2060–2075. (b) Zimmerman, H. E.; Bunce, R. A. *J. Org. Chem.* **1982**, *47*, 3377–3396.

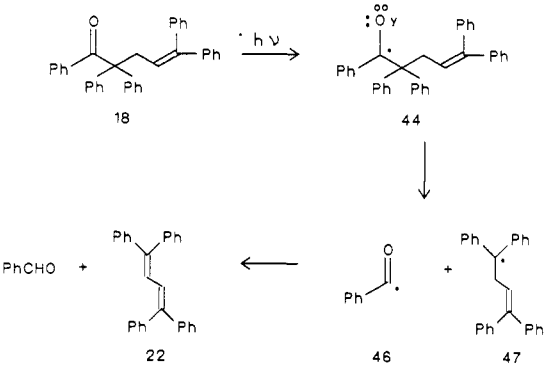
Scheme V. Rearrangement Mechanisms



Scheme VI. Reversion of Ketone 18 to Cyclopropanol Product



Scheme VII. Type I Fission of Pentaphenyl Ketone 18



is outlined in Scheme V. It needs to be recognized that the role of such mechanisms is to portray the molecular change in geometry and electron distribution as a reaction proceeds. The diradical and other structures drawn are meant to exist on the reaction hypersurface along the mechanistic pathway but are not necessarily meant to be energy minima.[4a,19] The ground states of reactants and products as well as excited states of reactants are minima. The diradicals of the di-π-methane rearrangement, in certain instances, are known to be minima[19d-f] but in others may possibly be[22] points on the reaction hypersurface.

Several further points require discussion. One is that the reaction of the hydroxyalkyl diradicals **37** and **43** (i.e., the 1,3-diradicals) have the potential to transfer a hydrogen atom from the hydroxyl oxygen to the other odd-electron carbon; this would directly engender ketones **19**, **28** and **9**. However, three-ring closure to cyclopropanol product occurs in preference to this alternative. This has precedence in 1,5-diradicals where hydrogen transfer is less than the overwhelming process observed.[23,24]

Another item of interest is the preferential formation of the stereoisomers of the cyclopropanols and (silyloxy)cyclopropanes with large groups trans. This has precedence in at least three previous examples.[3e,f,25]

Excited- versus Ground-State Three-Ring Opening Regioselectivities. There was observed a striking difference between the ground-state and photochemical regioselectivity of the opening of the cyclopropanols and derivatives (bond a cleavage versus bond b fission in Scheme III). The photochemical openings proceed essentially regioselectively with scission of bond b, bearing the diphenylvinyl moiety. In contrast, the thermal openings proceed with opening of both bonds with bond a being favored. Only a qualitative statement is possible since in the ground-state chemistry at most ca. 70% of the isolated product was characterizable.

The photochemical regioselectivity is understandable as a consequence of the excitation being initially in the low-energy diphenylvinyl chromophore, a factor not involved in the ground-state chemistry. In the ground-state opening, bond b opening is favored electronically in giving the more stable carbanion while bond a is favored sterically as a consequence of the fission of a tetrasubstituted bond.

Reversion of the Pentaphenyl Ketone 18 to Cyclopropanol. This unusual rearrangement is depicted in Scheme VI. The reaction has relatively little analogy[26] except where a β-amino substitutent is present.[27] A likely

(19) (a) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Grunewald, G. L.; Sherwin, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 3316–3323. (b) Whether the cyclopropyldicarbinyl diradicals of the di-π-methane rearrangement of bicyclic systems are energy minima apparently is controversial.[20] (c) It has been suggested by Paquette[20] that there is a direct conversion of excited bicyclic triplets of the benzonorbornadiene type to the 1,3-diradical without intervention of the bridged cyclopropyldicarbinyl diradical triplet being involved or an energy minimum. (d) However, an early spin-free calculation of the hypersurface of the extended Hückel type showed the excited cyclopropyldicarbinyl diradical to be an energy minimum.[3b] (e) In more recent efforts[21a] SCF-CI computation of the hypersurfaces of the di-π-methane rearrangements of bicyclic triplets has also shown the cyclopropyldicarbinyl diradical to be an energy minimum. (f) Borden and Davidson have reported[21b] an energy minimum for the parent triplet cyclopropyldicarbinyl diradical.

(20) (a) Paquette, L. A.; Bay, E. *J. Org. Chem.* **1982**, *47*, 4597–4599. (b) Paquette, L. A.; Varadarajan, A.; Bay, E. *J. Am. Chem. Soc.* **1984**, *106*, 6702–6708. (c) Paquette, L. A.; Bay, E. *J. Am. Chem. Soc.* **1984**, *106*, 6693–6701. (d) Paquette, L. A.; Burke, L. D. *J. Org. Chem.* **1987**, *52*, 2674–2679.

(21) (a) Zimmerman, H. E.; Moore, J. M., to be published. (b) Quenemoen, K.; Borden, W. T.; Davidson, E. R.; Feller, D. *J. Am. Chem. Soc.* **1985**, *105*, 5054–5059.

(22) For certain singlet rearrangements stereospecifity is observed and the reaction appears concerted. The stereochemistry is in agreement with a Möbius cyclic array of six orbitals. In these cases[3e-h] efforts are in progress to determine the nature of the cyclopropyldicarbinyl diradical.

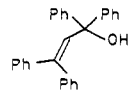
(23) Zimmerman, H. E.; Nuss, J. M. *J. Org. Chem.* **1986**, *51*, 4604–4617.

(24) Wagner, P. J.; Chiu, C. *J. Am. Chem. Soc.*, **1979**, *101*, 7134–7135.

(25) Zimmerman, H. E.; Schissel, D. N. *J. Org. Chem.* **1986**, *51*, 196–207.

(26) (a) In a study of a 11-keto steroid, Gull, Wehrli, and Jeger (Gull, P.; Wehrli, H.; Jeger, O. *Helv. Chim. Acta* **1971**, *54*, 2158–2166) observed photochemical formation of a product 9–11 bond formation and generation of a 9–11 bond. (b) 4-Propionyl- and 4-butanoylpyrimidine cyclize photochemically to the corresponding cyclopropanols as reported by: Alexander, E. C.; Jackson, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 5663–5665; *J. Am. Chem. Soc.* **1976**, *98*, 1609–1610.

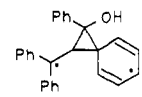
Chart I. Excited-State Reactivities



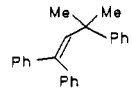
2

^1k_r = 9.31 × 10^7 s^{-1}
Ø = 0.0071
$^1k_{dt}$ = 1.33 × 10^{10} s^{-1}
M = 35

^1k_r = rate of reaction
$^1k_{dt}$ = total rate of decay
Ø = quantum yield
M = magic multiplier

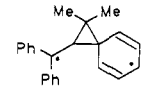


42



48

^1k_r = 1.9 × 10^9 s^{-1}
Ø = 0.036
$^1k_{dt}$ = 5.2 × 10^{10} s^{-1}
M = 202



49

mechanism for this reaction involves the unusual n-π* β-hydrogen abstraction followed by ring closure in analogy to the Yang reaction[28] forming cyclobutanols.

One interesting point is that microscopic reversibility does not hold in many photochemical systems. Thus cyclopropanol opening to give a ketone such as 18 is a π-π* reaction while the present reversion reaction involving hydrogen abstraction, is characteristically n-π*.

Mechanisms for Formation of Tetraphenylbutadiene 22. In a number of photolyses—that of the pentaphenyl diene 4, pentaphenyl cyclopropanol 14, and the pentaphenyl ketone 18—tetraphenylbutadiene (22) was observed as a minor product. In the case of irradiation of diene 4, one might consider expulsion of the phenyl hydroxy carbene from cyclopropyl dicarbinyl diradical 35. While this does have analogy,[13c,30,31] the tetraphenylbutadiene was not detected at low conversions of diene 4. As a second source of the diene, one can envisage a Griffin fragmentation[29] of the cyclopropanol photoproduct present at higher conversions. This mechanism would also hold in the photolysis starting with the cyclopropanol. However, the corresponding silyl ethers did not give rise to tetraphenylbutadiene, arguing against this mechanism.

Finally, in all cases where tetraphenylbutadiene was encountered, the pentaphenyl ketone 18 was also observed. This was found to proceed onward with facility to afford the observed tetraphenylbutadiene by a type I fission. This mechanism, shown in Scheme VII, must be utilized generally.

Excited Singlet Rate Comparisons. One final fascinating item is comparison of the excited singlet rates of tetraphenylpropenol 2 with those of the closely related 1,1,3-triphenyl-3-methyl-1-butene (48) studied by us earlier[13b] (Chart I). The rates of reaction differ by nearly 20 with the present system (i.e., 2) reacting more slowly. A possible source of this reactivity is greater molecular rigidity in 2 which would make it more difficult for phenyl–vinyl bridging. the lower "magic multiplier",[11a] M, is a measure of molecular rigidity and supports this supposition.

Conclusion. Despite being on the chemical scene for two decades, the di-π-methane rearrangement continues to provide new and useful transformations.

Experimental Section[32]

1,1,5,5-Tetraphenyl-3-methyl-1,4-pentadien-3-ol (3). To 28.0 mL (19.9 mmol) of a 0.71 M ethereal methyllithium solution at 0 °C was added 4.00 g (10.4 mmol) of 1,1,5,5-tetraphenyl-1,4-pentadien-3-one[35] in 150 mL of tetrahydrofuran. The mixture was stirred for 10.5 h and was allowed to warm to room temperature. Workup A[32] yielded 4.57 g of a viscous red-brown oil. Recrystallization from ether/pentane yielded 1.29 g (30.9%) of 3 as crystals, mp 89–91 °C.

Spectral data for 3: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.98–7.39 (m, 20 H, Ar), 6.09 (s, 2 H, vinyl), 1.84 (s, 1 H, OH), 1.44 (s, 3 H, CH_3); MS, *m/e* 402.2010 (calcd for $C_{30}H_{26}O$, *m/e* 402.1984); UV (CH_3CN) λ_{max} (nm) 257 (ε 23 200).

Anal. Calcd for $C_{30}H_{26}O$: C, 89.51; H 6.51. Found: C, 89.19; H, 6.63.

1,1,3,5,5-Pentaphenyl-1,4-pentadien-3-ol (4). To 5.2 mL (7.8 mmol) of 1.5 M *n*-butyllithium in hexane and 10 mL of ether was added dropwise at 0 °C 810 μL (1.22 g, 7.8 mmol) of bromobenzene in 10 mL of ether. The mixture was stirred for 40 min at 0 °C and then 2.00 g (5.2 mmol) of 1,1,5,5-tetraphenyl-1,4-pentadiene-3-one[35] in 75 mL of tetrahydrofuran was added. The mixture was stirred for 19.3 h. Workup A afforded 3.13 g of a brown oil. Decolorization and recrystallization from ether/pentane yielded 855 mg (35.4%) of 4, mp 119–122 °C.

Spectral data for 4: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.96–7.47 (m, 25 H, Ar), 6.44 (s, 2 H, vinyl), 2.18 (s, 1 H, OH); MS, [[M − OH)$^+$] *m/e* 447.2110 (calcd for $C_{35}H_{27}$ *m/e* 447.2113); UV (CH_3CN) λ_{max} (nm) 257 (ε 22 300).

Anal. Calcd for $C_{35}H_{28}O$: C, 90.48; H, 6.08. Found: C, 90.26; H, 6.27.

1-[(Phenyldimethylsilyl)oxy]-1,1,3,3-tetraphenyl-2-propene (5). To a stirred solution of 0.110 g (0.091 mmol) of 4-(*N,N*-dimethylamino)pyridine,[36] 0.613 mL (633 mg, 3.71 mmol) of dimethylphenylsilyl chloride, and 0.950 mL (625 mg, 6.18 mmol) of triethylamine in 10.0 mL of methylene chloride was added 1.12 g (3.09 mmol) of 1,1,3,3-tetraphenyl-2-propen-1-ol[5] in 10.0 mL of methylene chloride and the resulting mixture stirred for 36.0 h. Workup C gave 1.44 g of a viscous red oil, which was dissolved in ether and filtered through a 4-cm plug of alumina to afford 1.26 g (85%) of 5 as a colorless oil. Recrystallization from methanol yielded 0.750 g (57%) of the silyl ether as colorless needles, mp 71.5–73 °C.

Spectral data for 5: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.85–7.35 (m, 25 H, Ar), 6.74 (s, 1 H, vinyl), 0.02 (s, 6 H, CH_3); UV (EtOH) λ_{max} (nm) 260 (ε 18 500), 270 (12 000), 290 (6400); MS, *m/e* 496.2231 (calcd for $C_{35}H_{32}SiO$, *m/e* 496.2222).

Anal. Calcd for $C_{35}H_{32}SiO$: C, 84.63; H, 6.49. Found: C, 84.79; H, 6.62.

1,1,5,5-Tetraphenyl-3-methyl-3-[(phenyldimethylsilyl)oxy]-1,4-pentadiene (6). To 1.08 mL (714 mg, 7.06 mmol) of

(27) (a) A very large number of β-amino ketones are known to lead to cyclopropanols via a charge-transfer mechanism:[27b-g] (b) Roth, H. J.; El Raie, M. H. *Tetrahedron Lett.* **1970**, 2445–2446. (c) Roth, H. J.; ElRaie, M. H.; Schrauth, T. *Arch. Pharm.* **1974**, *307*, 584–595. (d) Rotter, F.; Abdul-Baki, A.; Schrauth, T.; Roth, H. J. *Arch. Pharm.* **1978**, *311*, 341–345; (e) 346–351. (f) Haber, H.; Buchholz, H.; Sukale, R.; Henning, H.-G. *J. Prakt. Chem.* **1985**, *327*, 51–62. (g) Padwa, A.; Gruber, R. *J. Am. Chem. Soc.* **1970**, *92*, 107–114.

(28) (a) Yang, N. C.; Elliot, S. P. *J. Am. Chem. Soc.* **1969**, *91*, 7550–7551. (b) Yang, N. C.; Elliott, S. P.; Kim, B. *J. Am. Chem. Soc.* **1969**, *91*, 7551–7553.

(29) Griffin, G. W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 537–547.

(30) Not only is there close analogy in the photochemistry of 3,3-dimethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene[13c] but also in the formation of diphenyl carbene and biphenyl in the irradiation of tetraphenylmethane[31a] and in the the elegant studies of Iwamura[31b] in which a formal di-π-methane rearrangement was shown to proceed by benzo–benzo bridging followed by carbene expulsion.

(31) (a) Walsh, T. D.; Powers, D. R. *Tetrahedron Lett.* **1970**, 3855–3856. (b) Iwamura, H.; Yoshimura, K. *J. Am. Chem. Soc.* **1974**, *96*, 2652–2654.

(32) Workup A refers to quenching the reaction by pouring it into a mixture of ice and staturated ammonium chloride solution, separating the layers, extracting the aqueous layer with ether or methylene chloride, washing the combined organic layers with water and brine, drying, filtering, and concentrating under vacuum. Workup B involves quenching the reaction by pouring it into a ice–water mixture and then continuing with the workup procedure in workup A. Workup C is similar to workup B but with a 5% aqueous hydrochloric acid wash after ether extraction. All photolyses were thoroughly purged with purified nitrogen[34] both prior to and during photolysis. Exploratory used a Hanovia 450-W medium pressure lamp with the appropriate filter.

(33) Zimmerman, H. E.; Ramsden, W. R.; King, R. K., unpublished results.

(34) Meites, L.; Meites, T. *Anal. Chem.* **1948**, *20*, 984–985.

(35) (a) Marin, G.; Chodkiewicz, W.; Cadiot, P.; Willemart, A. *Bull. Soc. Chem. Fr.* **1958**, 1594–1597. (b) See ref 13c for a further modification.

(36) Chaudhary, S. K.; Hernandez, O. *Tetrahedron Lett.* **1979**, 99–102.

triethylamine, 700 μL (724 mg, 4.24 mmol) of phenyldimethylchlorosilane, and 85 mg (710 μmol) of 4-(*N*,*N*-dimethylamino)pyridine[36] in 10 mL of methylene chloride was added 1.42 g (3.53 mmol) of 1,1,5,5-tetraphenyl-3-methyl-1,4-pentadien-3-ol in 20 mL of methylene chloride. The mixture was stirred for 15 h at room temperature. Workup B[32] followed by crystallization from methylene chloride/pentane yielded 1.42 g of the impure silyl ether, mp 108–111 °C. Recrystallization at room temperature twice from methylene chloride/pentane yielded 1.30 g (68.6%) of **6**, mp 111–112 °C.

Spectral data for **6**: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.84–7.51 (m, 25 H, Ar), 5.96 (s, 2 H, vinyl), 1.25 (s, 3 H, CH_3), 0.18 (s, 6 H, $SiCH_3$); MS, *m/e* 536.2535 (calcd for $C_{38}H_{36}OSi$, *m/e* 536.2535); UV (CH_3CN) λ_{max} (nm) 254 (ε 21 600).

Anal. Calcd for $C_{38}H_{36}OSi$: C, 85.03; H, 6.76. Found: C, 85.20; H, 6.63.

1,1,3,5,5-Pentaphenyl-3-[(phenyldimethylsilyl)oxy]-1,4-pentadiene (7). To 730 μL (482 mg, 4.76 mmol) of triethylamine, 95 mg (77.8 μmol) of 4-(*N*,*N*-dimethylamino)pyridine,[36] and 475 μL (488 mg, 2.86 mmol) of phenyldimethylchlorosilane in 20 mL of methylene chloride was added at room temperature 1.10 g (2.38 mmol) of 1,1,3,5,5-pentaphenyl-1,4-pentadien-3-ol in 10 mL of methylene chloride. The mixture was stirred for 25 h. Workup B yielded 1.51 g of a brown oil. The oil in methylene chloride was applied to a pad of neutral alumina and eluted with 500 mL of a 20% methylene chloride/pentane. The filtrate was concentrated under vacuum to yield 1.22 g of a clear oil. Recrystallization from methylene chloride/pentane yielded 950 mg (66.8%) of **7** as clear crystals, mp 126–127 °C.

Spectral data for **7**: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.66–7.46 (m, 30 H, Ar), 6.14 (s, 2 H, vinyl), 0.03 (s, 6 H, $Si(CH_3)_2$); MS, *m/e* 598.2696 (calcd for $C_{43}H_{38}OSi$, *m/e* 598.2692); UV (CH_3CN) λ_{max} (nm) 255 (ε 26 900).

Anal. Calcd for $C_{43}H_{38}OSi$: C, 86.24; H, 6.40. Found: C, 86.44; H, 6.36.

Exploratory Direct Photolysis of 1,1,3,3-Tetraphenyl-2-propen-1-ol (2). A solution of 275 mg (760 μmol, 2.81×10^{-3} M) of 1,1,3,3-tetraphenyl-2-propen-1-ol[5] in 270 mL of *tert*-butyl alcohol was irradiated for 8.0 h through a Corex filter with a 450-W Hanovia medium-pressure lamp. After concentration of the photolysate under vacuum, 270-MHz NMR analysis revealed that approximately 75% of the starting material had been converted to one photoproduct. Trituration of the photolysate with hexane several times led to 100.5 mg (36%) of *cis*-1,2,2,3-triphenylcyclopropan-1-ol (**8**), mp 110–117 °C, as a yellow solid. Trituration of this solid from pentane gave 45.4 mg (13%) of the cyclopropanol as a light yellow solid, mp 121–124 °C, sensitive to ring opening.

Spectral data for **8**: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.90–7.40 (m, 20 H, Ar), 3.64 (s, 1 H, CHPh), 2.28 (s, 1 H, OH); UV (EtOH) λ_{max} (nm) 270 (ε 975), 290 (200); MS, *m/e* 362.1667 (calcd for $C_{27}H_{22}O$, *m/e* 362.1671).

Anal. Calcd for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.69; H, 6.43.

Degradation of *cis*-1,2,2,3-Tetraphenylcyclopropan-1-ol (8). A solution of 53.0 mg (146 μmol) of *cis*-1,2,2,3-tetraphenylcyclopropan-1-ol, 45.0 mg (833 μmol) of sodium methoxide, and 10.0 mL of methanol was stirred for 3.0 h. Workup B afforded 50.3 mg (95%) of 1,2,3,3-tetraphenyl-1-propanone as a light yellow solid, mp 177–181 °C. Recrystallization from ether gave 38.6 mg (73%) of the ketone as colorless plates, mp 183–185 °C, identical with material obtained from independent synthesis (vide infra).

1,2,3,3-Tetraphenyl-1-propanone (9). A solution of 1.32 g (5.10 mmol) of benzhydryl bromide, 0.685 g (6.12 mmol) of potassium *tert*-butoxide, and 0.500 g (2.55 mmol) of deoxybenzoin[37] in 40.0 mL of tetrahydrofuran was stirred at 90 °C for 3 days. Workup B afforded 1.45 g of a waxy yellow solid, which was chromatographed on a 2 × 75 cm silica gel column, and 500-mL ether/hexane fractions were collected. Fraction 7 gave 98.0 mg (11%) of 1,2,3,3-tetraphenyl-1-propanone as a light yellow solid. Recrystallization from ether afforded 56.0 mg (6%) of the ketone as colorless plates, mp 185–187 °C, identical with material obtained from the degradation of *cis*-1,2,2,3-tetraphenyl-1-cyclopropanol.

Spectral data for **9**: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.02–7.85 (m, 20 H, Ar), 5.46 (d, *J* = 12 Hz, 1 H, Ph_2CH), 4.93 (d, *J* = 12 Hz, 1 H, CHPh); MS, *m/e* 362.1672 (calcd for $C_{27}H_{22}O$, *m/e* 362.1671).

Anal. Calcd for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.82; H, 6.43.

***trans*-1,2,2,3-Tetraphenylcyclopropan-1-ol (11).** To a stirred solution of 250 mg (726 μmol) 1,2,3,3-tetraphenylcyclopropene[38] in 10 mL of tetrahydrofuran at 0 °C was added 7.60 mL (7.60 mmol) of borane–tetrahydrofuran (1 M in tetrahydrofuran) dropwise. The mixture was allowed to warm to room temperature and stirred for 12.0 h. This was cooled to 0 °C and 5.70 mL (28.5 mmol) of 5.0 M aqueous sodium acetate was cautiously added, followed by 2.3 mL (20.3 mmol) of 30% aqueous hydrogen peroxide.[6] After the mixture was stirred at 0 °C for 1.5 h, workup B gave 265 mg of slightly yellow foam. Trituration of this foam with hexane gave 140 mg (53%) of *trans*-1,2,2,3-tetraphenylcyclopropan-1-ol as a colorless solid, mp 64–69 °C. Recrystallization from ether/pentane afforded 95.0 mg (20%) of the cyclopropanol as a colorless solid, mp 71–73 °C (sealed tube).

Spectral data for **11**: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.85–7.65 (m, 20 H, Ar), 3.43 (s, 1 H, CHPh), 2.35 (s, 1 H, OH); MS, *m/e* 362.1654 (calcd for $C_{27}H_{22}O$, *m/e* 362.1671).

Anal. Calcd for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.81; H, 6.49.

Exploratory Direct Photolysis of 1-[(Phenyldimethylsilyl)oxy]-1,1,3,3-tetraphenyl-2-propene (5). A solution of 215 mg (433 μmol, 1.73×10^{-3} M) of **5** in 250 mL of acetonitrile was irradiated for 8.0 h through a Corex filter with a 450-W Hanovia medium-pressure lamp. Concentration under vacuum gave 245 mg of a dark brown oil, which was chromatographed on a 20 × 20 cm preparative silica gel plate, eluting four times with 0.5% ether/pentane. The fastest moving band afforded 134 mg (62%) of *cis*-1-[(phenyldimethylsilyl)oxy]-1,2,3,3-tetraphenylcyclopropane (**13**) as a light yellow oil, which was further purified by preparative HPLC (50 × 0.95 cm silica column, 2% ether/pentane) to afford 112 mg (52%) of the cyclopropane as a colorless oil. Band 2 contained 45.0 mg (20%) of **5** as a colorless oil.

Spectral data for **13**: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.65–7.75 (m, 25 H, Ar), 3.66 (s, 1 H, CHPh), –0.19 (s, 3 H, CH_3), –0.28 (s, 3 H, CH_3); UV (EtOH) λ_{max} (nm) 250 (ε 1050), 270 (450), 280 (200); MS, *m/e* 496.2214 (calcd for $C_{35}H_{32}SiO$, *m/e* 496.2222).

Anal. Calcd for $C_{35}H_{32}SiO$: C, 84.63; H, 6.49. Found: C, 84.57; H, 6.69.

***cis*-1-[(Phenyldimethylsilyl)oxy]-1,2,3,3-tetraphenylcyclopropane (13).** To a stirred solution of 15.4 mg (13 μmol) of 4-(*N*,*N*-dimethylamino)pyridine,[36] 85.0 μL of dimethylphenylsilyl chloride (87.1 mg, 510 μmol), and 126 μL (83 mg, 820 μmol) of triethylamine in 10.0 mL of methylene chloride was added 149 mg (410 μmol) of *cis*-1,2,3,3-tetraphenylcyclopropan-1-ol in 10.0 mL of methylene chloride and the resulting mixture stirred for 48 h. Workup B gave 162 mg of a dark brown oil, which was chromatographed on a 20 × 20 cm preparative thin-layer silica gel plate, eluting with 2% ether/pentane to give two major bands. The fastest moving band gave 45.4 mg (22%) of **13**, a colorless oil identical with the material isolated from the photolysis of 1-[(phenyldimethylsilyl)oxy]-1,1,3,3-tetraphenyl-2-propene (vide supra). Band 2 gave 37.0 mg (25%) of 1,2,3,3-tetraphenyl-1-propanone as a colorless white solid, mp 180–185 °C.

Exploratory Acetophenone-Sensitized Photolysis of 1,1,3,3-Tetraphenyl-2-propen-1-ol (2). A solution of 181 mg (500 μmol) of **2** and 15.0 mL (125 mmol) of acetophenone in 270 mL of *tert*-butyl alcohol was irradiated for 6.0 h through a Pyrex filter with a 450-W Hanovia medium-pressure lamp. The photolysate was then concentrated under vacuum and the acetophenone removed (40 °C, 0.15 Torr) to afford 205 mg (105%) of a yellow solid. NMR analysis showed the presence of only reactant **2** and no cyclopropanol.

Exploratory Direct Photolysis of 1,1,3,5,5-Pentaphenyl-1,4-pentadien-3-ol (4). A solution of 208.4 mg (449 μmol, 1.80×10^{-3} M) of 1,1,3,5,5-pentaphenyl-1,4-pentadien-3-ol in 250 mL of acetonitrile was photolyzed through a Pyrex filter for 5.2 h with a 450-W Hanovia medium-pressure lamp. The photolysate was

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concentrated under vacuum to yield 225.5 mg of a mixture whose NMR showed a 8.1:4.4:1 ratio of *cis*-1-hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane to *trans*-1-hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane to 1,2,2,5,5-pentaphenyl-4-penten-1-one. The mixture was subjected to preparative HPLC (50 × 0.95 cm silica column, 15% ether/pentane) to give the following fractions: 1, 15.8 mg (9.82%) of slightly impure 1,1,4,4-tetraphenyl-1,3-butadiene, which was recrystallized to yield 2.2 mg (1.4%) of the compound, mp 195–197 °C (lit.[39] mp 200 °C), pure by NMR; 2, 19.5 mg of unidentified aromatic material; 3, 27.2 mg of a mixture of compounds including 1,2,2,5,5-pentaphenyl-4-penten-1-one, which was recrystallized from pentane in a 3.7-mg (1.7%) yield, mp 168–169 °C; 4, 76.3 mg (36.5%) of *cis*-1-hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane (**14**) as a foam.

Spectral data for **14**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.88–7.61 (m, 25 H, Ar), 6.02 (d, J = 9.7 Hz, 1 H, vinyl), 3.19 (d, J = 9.7 Hz, 1 H, cyclopropyl), 2.55 (br s, 1 H, OH); MS, m/e 464.2136 (calcd for $C_{35}H_{28}O$ 464.2140); UV (CH_3CN) λ_{max} (nm) 255 (ε 15 600).

Fraction 5 contained 30.0 mg (14.4%) of *trans*-1-hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane (**15**) as a foam.

Spectral data for **15**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.94–7.66 (m, 25 H, Ar), 5.95 (d, J = 9.9 Hz, 1 H, vinyl), 2.86 (d, J = 9.9 Hz, 1 H, cyclopropyl), 2.16 (br s, 1 H, OH); MS, m/e 464.2146 (calcd for $C_{35}H_{28}O$, m/e 464.2140); UV (CH_3CN) λ_{max} (nm) 255 (ε 15 400).

Exploratory Direct Photolysis of 1,1,3,5,5-Pentaphenyl-3-[(phenyldimethylsilyl)oxy]-1,4-pentadiene (7). A solution of 110.2 mg (184 μmol, 7.36 × 10^{-4} M) of 1,1,3,5,5-pentaphenyl-3-[(phenyldimethylsilyl)oxy]-1,4-pentadiene in 250 mL of acetonitrile was photolyzed for 2.3 h with a 450-W Hanovia medium-pressure lamp. The photolysate was concentrated under vacuum to yield 111.8 mg of a mixture that contained a 1.4:1 ratio of *trans*-1,2,2-triphenyl-1-[(phenyldimethylsilyl)oxy]-3-(2,2-diphenylvinyl)cyclopropane (**17**) to *cis*-1,2,2-triphenyl-1-[(phenyldimethylsilyl)oxy]-3-(2,2-diphenylvinyl)cyclopropane (**16**) by NMR. Fractional crystallization from ether of this mixture gave 38.8 mg (35.3%) of **17**, mp 176–178 °C, which was recrystallized from ether/pentane to yield 30.0 mg (27.2%), mp 178–179 °C.

Spectral data for **17**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.74–7.72 (m, 30 H, Ar), 5.91 (d, J = 11.2 Hz, 1 H, vinyl), 2.94 (d, J = 11.2 Hz, 1 H, cyclopropyl), −0.23 (s, 3 H, $SiCH_3$), −0.28 (s, 3 H, $SiCH_3$); MS, m/e 598.2655 (calcd for $C_{43}H_{38}OSi$, m/e 598.2692); UV (CH_3CN) λ_{max} (nm) 273 (ε 16 800).

Anal. Calcd for $C_{43}H_{38}OSi$: C, 86.24; H, 6.40. Found C, 85.87; H, 6.54.

The filtrate was subjected to HPLC (50 × 0.95 cm silica column, 1.5% ether/pentane) to give the following fractions: 1, 5.1 mg of unidentified aromatic materials; 2, 33.8 mg (30.9%) of **16**, mp 165–167 °C, which was recrystallized from ether/pentane to give product, mp 168–169.5 °C.

Spectral data for **16**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.70–7.66 (m, 30 H, Ar), 5.82 (d, J = 10.3 Hz, 1 H, vinyl), 3.21 (d, J = 10.3 Hz, 1 H, cyclopropyl), 0.15 (s, 3 H, $SiCH_3$), 0.09 (s, 3 H, $SiCH_3$); MS, m/e 598.2695 (calcd for $C_{43}H_{38}OSi$, m/e 598.2692); UV (CH_3CN) λ_{max} (nm) 271 (ε 19 200).

Anal. Calcd for $C_{43}H_{38}OSi$: C, 86.24; H, 6.40. Found: C, 86.29; H, 6.39.

Fraction 3 contained 11.4 mg (10.3%) of the trans cyclopropane, mp 178–179 °C.

Reaction of *cis*-1-Hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane (14) with Sodium Methoxide. A solution of 33.0 mg (71.1 μmol) of *cis*-1-hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane and 34.8 mg (718 μmol) of sodium methoxide in 25 mL of methanol was stirred for 5 h. Workup A gave 31.5 mg of an oil, whose NMR showed a 5.3:1 mixture of 1,4,4-triphenyl-2-(1,1-diphenylmethyl)-3-buten-1-one (**19**) to 1,2,2,5,5-pentaphenyl-4-penten-1-one (**18**). Crystallization of the mixture from ether/pentane gave 11.7 mg (35.4%) of **19**, mp 143–147 °C. The filtrate was subjected to HPLC (50 × 0.95 cm silica column, 4% ether/pentane) to give the following fractions: 1, 2.3 mg of unidentified material; 2, 2.3 mg (7.0%) of **18**, which was recrystallized from ether/pentane to yield 2.1 mg (6.36%) of clear crystals, mp 171–173 °C; 3, 4.9 mg (15%) of **19**, which was recrystallized from ether/pentane to give 2.5 mg (7.5%) of the ketone as a fluffy white solid, mp 149–150 °C, bringing the yield to 16.6 mg (50%).

Reaction of *trans*-1-Hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane (15) with Sodium Methoxide. A solution of 30.8 mg (66.3 μmol) of *trans*-1-hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane and 32.8 mg (607 μmol) of sodium methoxide in 25 mL of methanol was stirred for 4 h. Workup A gave 28.4 mg of a mixture which included a 1:1 ratio of 1,4,4-triphenyl-2-(1,1-diphenylmethyl)-3-buten-1-one (**19**) to 1,2,2,5,5-pentaphenyl-4-penten-1-one (**18**). The mixture was subjected to HPLC (50 × 0.95 cm silica column, 4% ether/pentane) to give the following fractions: 1, 7.6 mg (27.4%) of 1,2,2,5,5-pentaphenyl-4-penten-1-one (**18**), which was recrystallized with ether/pentane to yield 3.1 mg (10.1%) of crystalline ketone, mp 169–170 °C; 2, 5.0 mg of unidentifiable material; 3, 6.3 mg (19.1%) of **19**, which was recrystallized to give 3.9 mg (11.8%) of the fluffy white ketone, mp 149–150 °C.

Reaction of *cis*-1,2,2-Triphenyl-1-[(phenyldimethylsilyl)oxy]-3-(2,2-diphenylvinyl)cyclopropane (16) with Tetrabutylammonium Fluoride. A solution of 20 mg (33.4 μmol) of *cis*-1,2,2-triphenyl-1-[(phenyldimethylsilyl)oxy]-3-(2,2-diphenylvinyl)cyclopropane in 20 mL of tetrahydrofuran and 35 μL (35 μmol) of a 1.0 M (in tetrahydrofuran) solution of tetrabutylammonium fluoride was stirred for 20 min. Workup A gave 19.1 mg of a mixture of compounds that included a 5:1 ratio of 1,4,4-triphenyl-2-(1,1-diphenylmethyl)-3-buten-1-one (**19**) to 1,2,2,5,5-pentaphenyl-4-penten-1-one (**18**) by NMR. Separation by means of HPLC (50 × 0.95 cm silica column, 5% ether/pentane) gave the following fractions: 1, 1.2 mg (7.8%) of **18**; 2, 5.1 mg of an unknown compound; 3, 4.2 mg (27.1%) of **19**, which was recrystallized from ether/pentane to yield 3.2 mg (20.6%), mp 148.5–150 °C.

Reaction of *trans*-1,2,2-Triphenyl-1-[(phenyldimethylsilyl)oxy]-3-(2,2-diphenylvinyl)cyclopropane (17) with Tetrabutylammonium Fluoride. A solution of 29.0 mg (48.5 μmol) of *trans*-1,2,2-triphenyl-1-[(phenyldimethylsilyl)oxy]-3-(2,2-diphenylvinyl)cyclopropane in 20 mL of tetrahydrofuran and 50 μL (50 μmol) of a 1 M (in tetrahydrofuran) tetrabutylammonium fluoride solution was stirred for 20 min. Workup A gave 25.1 mg of a mixture of compounds that included a 6.6:1 ratio of 1,4,4-triphenyl-2-(1,1-diphenylmethyl)-3-buten-1-one (**19**) to 1,2,2,5,5-pentaphenyl-4-penten-1-one (**18**) by NMR. Separation by means of HPLC (50 × 0.95 cm silica column, 5% ether/pentane) gave the following fractions: 1, 3.5 mg (15.5%) of **18**, which was recrystallized from ether/pentane to yield 2.6 mg (11.5%) of a colorless solid, mp 169–171 °C; 2, 5.5 mg of an unknown compound; 3, 8.5 mg (37.7%) of **19**, which was recrystallized to give 7.9 mg (35.1%) of fluffy white crystals, mp 149–150 °C.

1,2,2,5,5-Pentaphenyl-4-penten-1-one (18). A solution of 305 mg (2.71 mmol) of potassium *tert*-butoxide in 30 mL of *tert*-butyl alcohol and 500 mg (1.84 mmol) of 1,2,2-triphenylethanone[40] in 20 mL of tetrahydrofuran was refluxed for 20 min. Then 554.5 mg (2.03 mmol) of 1-bromo-3,3-diphenyl-2-propene[41] in 10 mL of tetrahydrofuran was added, and the mixture was refluxed for 1.5 h. Workup A yielded 815 mg of a solid, which was chromatographed on a 60 × 4 cm column slurry packed with silica gel. Elution was with 5% ether/hexane and 200-mL fractions. Fractions 4–5 yielded 497 mg (58.2%) of **18** as a white solid, which was recrystallized from ether/pentane to yield 363 mg (42.5%) of compound, mp 172–173 °C.

Spectral data for **18**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.71–7.79 (m, 25 H, Ar), 5.88 (t, J = 7.0 Hz, 1 H, vinyl), 3.29 (d, J = 7.0 Hz, 2 H, CH_2); MS, m/e 464.2129 (calcd for $C_{35}H_{28}O$, m/e 464.2140); UV (CH_3CN) λ_{max} (nm) 254 (ε 17 400).

Anal. Calcd for $C_{35}H_{28}O$: C, 90.48; H, 6.08. Found: C, 90.22; H, 6.09.

1,4,4-Triphenyl-2-(1,1-diphenylmethyl)-3-buten-1-one (19). To 282 mg (2.52 mmol) of potassium *tert*-butoxide in 10 mL of *tert*-butyl alcohol was added 500 mg (1.68 mmol) of 1,4,4-tri-

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phenyl-3-buten-1-one[42] as a solid. The mixture was refluxed for 30 min, and then 456 mg (1.84 mmol) of benzhydryl bromide in 22 mL of *tert*-butyl alcohol was added. The mixture was refluxed for 14.25 h and stirred for 16 h at room temperature. Workup A yielded a solid, which was chromatographed on a 40 × 4 cm column slurry packed with silica gel. Elution with 5% ether/hexane and 400-mL fractions gave fraction 2, 447 mg (57.3%) of **19** as a fluffy white solid, which was recrystallized from ether/pentane to yield 285 mg (36.6%) of analytically pure material, mp 146–148 °C.

Spectral data for **19**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.53–7.50 (m, 25 H, Ar), 6.06 (d, J = 10.1 Hz, 1 H, vinyl), 4.99 (m, 1 H, CH), 4.77 (d, J = 11.0 Hz, 1 H, benzhydryl); MS, m/e 464.2136 (calcd for $C_{35}H_{28}O$, m/e 464.2140).

Anal. Calcd for $C_{35}H_{28}O$: C, 90.48; H, 6.08. Found C, 90.28; H, 6.16.

Single-Crystal X-ray of *cis*-1,2,2-Triphenyl-1-[(phenyldimethylsilyl)oxy]-3-(2,2-diphenylvinyl)cyclopropane (16). Crystals of *cis*-1,2,2-triphenyl-1-[(phenyldimethylsilyl)oxy]-3-(2,2-diphenylvinyl)cyclopropane were prepared by slow crystallization from methylene chloride/hexane. Preliminary examinations and collection of data were carried out on a Nicolet (Syntex) P$\bar{1}$ diffractometer using a graphite monochromated Mo Kα radiation source from a crystal of dimensions of 0.2 × 0.2 × 0.2 mm. The intensities of four standard reflections did not vary by more than 3% during data collection. The structure, consisting of one independent molecule, was solved under triclinic P$\bar{1}$ symmetry by direct methods with the MULTAN 80 package[43] and refined by least squares. Anisotropic thermal parameters were used for all non-hydrogen atoms, while isotropic thermal parameters were used for the hydrogen atoms. The final R_1 and $R_w(F)$ values converged at 0.100 and 0.098, respectively. Results and structural parameters are summarized in the supplementary material.

Partial Conversion Exploratory Direct Photolysis of 1,1,3,5,5-Pentaphenyl-1,4-pentadien-3-ol (4). A solution of 104 mg (224 μmol, 1.18 × 10^{-3} M) of 1,1,3,5,5-pentaphenyl-1,4-pentadien-3-ol in 190 mL of acetonitrile was photolyzed through a Pyrex filter for 1 h with a 450-W Hanovia medium-pressure lamp. The photolysate was concentrated under vacuum to yield 108 mg of a mixture of compounds whose NMR showed a 8.7:4.0:1 ratio of the starting dienol to *cis*-1-hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane (**14**) to *trans*-1-hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane (**15**). The photolysate was subjected to HPLC system (50 × 0.95 cm silica column, 15% ether/pentane) to give the following fractions: 1, 2.0 mg of aromatic compounds (1,1,4,4-tetraphenyl-1,3-butadiene was not detected by NMR) present); 2, 59.3 mg (57.1%) of the starting dienol which was pure by NMR; 3, 26.1 mg (25.1%) of **14**; 4, 7.0 mg (6.70%) of **15**.

Stability of *cis*- and *trans*-1-Hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane (14 and 15) under Photolysis Conditions. A solution of 103 mg (223 μmol, 1.24 × 10^{-3} M) of 1,1,3,5,5-pentaphenyl-1,4-pentadien-3-ol (**4**) in 180 mL of acetonitrile was photolyzed for 30 min through a Pyrex filter with a 450-W Hanovia medium-pressure lamp. A 35.0 mg (211 μmol) sample of fluorene added as internal standard followed by concentration under vacuum to leave 149 mg. NMR analysis of the mixture showed 1.60 μmol of 1,2,2,5,5-pentaphenyl-4-penten-1-one (**18**), 67.1 μmol of *cis*-1-hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane (**14**), 21.0 μmol of *trans*-1-hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane (**15**), and 94.5 μmol of **4** (82.6% mass balance). The mixture was stirred for 5.5 h in 150 mL of acetonitrile and then concentrated below 45 °C under vacuum to yield 149.1 mg of material. NMR analysis showed 1.67 μmol of **18**, 63.3 μmol of **14**, 19.5 μmol of **15**, and 98.3 μmol of **4** (82.0% mass balance). Thus within experimental error no cyclopropanol opening occurred.

Exploratory Sensitized Photolysis of 1,1,3,5,5-Pentaphenyl-1,4-pentadien-3-ol (4). A solution of 109 mg (235 μmol, 1.24 × 10^{-3} M) of 1,1,3,5,5-pentaphenyl-1,4-pentadien-3-ol and 63.5 (282 μmol, 1.48 × 10^{-3} *M*) of 4-(*N*,*N*-dimethylamino)-benzophenone in 190 mL of acetonitrile was photolyzed for 40 min through a Pyrex filter and a 1.4 × 10^{-2} M sodium metavanadate filter solution (cutoff 330 nm) circulated through the cooling jacket of the 450-W Hanovia medium-pressure lamp. The photolysate was concentrated under vacuum to yield 188.8 mg of an oil, which was subjected to HPLC (8 × 0.95 cm silica precolumn in series with a 50 × 0.95 cm silica column, 30% ether/pentane) to give the following fractions: 1, of 15.4 mg (18.3%) of impure 1,1,4,4-tetraphenyl-1,3-butadiene, which was recrystallized from ether/pentane to yield 4.7 mg (4.65%) of the pure butadiene, mp 196–198 °C (lit.[39] mp 200 °C); 2, 50.5 mg of a mixture of compounds including *cis*-1-hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane (**14**) and 1,2,2,5,5-pentaphenyl-4-penten-1-one (**18**); 3, 25.9 mg (23.7%) of *trans*-1-hydroxy-1-phenyl-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane; 4, 9.3 mg of unidentified aromatic compounds; 5, contained 52.7 mg (234 μmol) of 4-(*N*,*N*-dimethylamino)benzophenone. Fraction 2 was subjected to HPLC twice more (50 × 0.95 cm silica column, 15%, 4% ether/pentane to yield 19.5 mg (17.9%) of **14** and 4.5 mg (4.12%) of slightly impure **18**, which was recrystallized from ether/pentane to yield 1.7 mg (1.56%) of the ketone, mp 169–169.5 °C.

Exploratory Sensitized Photolysis of 1,1,3,5,5-Pentaphenyl-3-[(phenyldimethylsilyl)oxy]-1,4-pentadiene (7). A solution of 144.1 mg (241 μmol, 9.64 × 10^{-4} M) of 1,1,3,5,5-pentaphenyl-3-[(phenyldimethylsilyl)oxy]-1,4-pentadiene and 118.9 mg (606 μmol, 2.42 × 10^{-3} M) of xanthone in 250 mL of acetonitrile was photolyzed for 35 min through a Pyrex filter and a 1.4 × 10^{-2} M sodium metavanadate filter solution (cutoff 330 nm) circulated through the cooling jacket of a 450-W Hanovia medium pressure lamp. The photolysate was concentrated under vacuum to yield 267.5 mg of a mixture of sensitizer and vinylcyclopropanes. The ratio of *trans*-1,2,2-triphenyl-1-[(phenyldimethylsilyl)oxy]-3-(2,2-diphenylvinyl)cyclopropane (**17**) to *cis*-1,2,2-triphenyl-1-[(phenyldimethylsilyl)oxy]-3-(2,2-diphenylvinyl)cyclopropane (**16**) by NMR was 2.6:1. The sensitizer was removed by HPLC (50 × 0.95 cm silica column, 25% ether/pentane) to give the following fractions: A1, 134.2 mg (92.3%) of a 2.4:1 mixture of trans to cis vinylcyclopropanes; A2, 114.5 mg (584 μmol) of xanthone. Fraction A1 was fractionally crystallized with ether to yield 91.4 mg (63.4%) of impure **17**, mp 168–171 °C. Recrystallization from ether/pentane yielded 51.6 mg (35.8%) of pure trans cyclopropane by NMR. The filtrate was subjected to HPLC (1.5% ether/pentane) to give three fractions: B1, 1.1 mg of unidentified material; B2, 26.0 mg (18.0%) of **16**, mp 166–167 °C; B3, 10.5 mg (7.30%) of the trans cyclopropane, which was recrystallized from ether/pentane to yield 7.9 mg (5.48%) of compound, mp 178–179 °C.

Exploratory Direct Photolysis of 1,1,5,5-Tetraphenyl-3-methyl-1,4-pentadien-3-ol (3). A solution of 209 mg (520 μmol, 2.17 × u0^{-3} M) of 1,1,5,5-tetraphenyl-3-methyl-1,4-pentadien-3-ol (**3**) in 240 mL of acetonitrile was photolyzed for 1.5 h through a Corex filter, with a 450-W Hanovia medium-pressure lamp. Concentration under vacuum yielded 221.4 mg of a yellow oil, whose NMR showed a 10:7.0:3.9:1 ratio of 3,3,6,6-tetraphenyl-5-hexen-2-one (**25**) to *cis*-1-hydroxy-1-methyl-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**23**) to *trans*-1-hydroxy-1-methyl-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**24**) to 1,1,5,5-tetraphenyl-3-methyl-1,4-pentadien-3-ol (**3**). The photolysate was stirred for 13 h in 17 mL of methylene chloride containing 31.2 mg (261 μmol) of 4-(*N*,*N*-dimethylamino)pyridine, 167 μL (110 mg, 1.09 mmol) of triethylamine, and 172 μL (178 mg, 1.04 mmol) of phenyldimethylchlorosilane.[36] Workup B yielded 339.5 mg of a brown oil, which was subjected to HPLC (8 × 0.95 cm silica precolumn in series with a 50 × 0.95 cm silica column, 10% ether/pentane) to give the following fractions: A1, 44.0 mg of silicon byproducts; A2, 82.6 mg (29.6%) of a mixture whose NMR showed a 5.1:3.3:1 ratio of *cis*-1-methyl-1-[(phenyldimethylsilyl)oxy]-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**26**) to *trans*-1-methyl-1-[(phenyldimethylsilyl)oxy]-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**27**) to 1,1,5,5-tetraphenyl-3-methyl-3-[(phenyldimethylsilyl)oxy]-1,4-pentadiene; A3, 12.0 mg

(42) Walborsky, H. M.; Plonsker, L. *J. Am. Chem. Soc.* **1961**, *83*, 2138–2144.

(43) (a) The MULTAN[14b] series of programs was used within a framework developed by C. Strouse of UCLA and modified by J. Moore and A. M. Weber, University of Wisconsin—Madison: (b) Germanin, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1971**, *A27*, 368–376.

of unidentified aromatic material; A4, 21.3 mg of unidentified aromatic material; A5, 46.4 mg (22.2%) of 3,3,6,6-tetraphenyl-5-hexen-2-one, mp 126–129 °C, which was recrystallized from ether/pentane to yield 26.2 mg (12.5%) of the compound, mp 130–132 °C (lit.[9] mp 131–133 °C). Fractional crystallization of fraction A2 from ether yielded 29.6 mg (10.7%) of **26**, mp 167–169 °C.

Spectral data for **26**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.77–7.54 (m, 25 H, Ar), 5.67 (d, J = 10.4 Hz, 1 H, vinyl), 2.23 (d, J = 10.4 Hz, 1 H, cyclopropyl), 1.28 (s, 3 H, CH_3), 0.40 (s, 3 H, $SiCH_3$), 0.39 (s, 3 H, $SiCH_3$); A NOE difference measurement[44] with irradiation of the methyl group led to a 13.5% increase in the cyclopropyl proton signal: MS, m/e 536.2538 (calcd for $C_{38}H_{36}OSi$ m/e 536.2535).

Anal. Calcd for $C_{38}H_{36}OSi$: C, 85.03; H, 6.76. Found: C, 84.82; H, 6.73.

The filtrate was subjected to HPLC (50 × 0.95 cm silica column, 1.5% ether/pentane) to give the following fractions: B1, 13.4 mg (6.41%) of a 1.1:1 mixture of cis cyclopropane to silyloxy diene; B2 (shaved from B1), 6.2 mg (2.5%) of a 5.9:1 mixture of cis cyclopropane to silyloxy diene; B3, 20.3 mg (7.3%) of **27** as an oil, which solidified upon refrigeration, mp 127–128.5 °C.

Spectral data for **27**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.02–7.44 (m, 25 H, Ar), 5.53 (d, J = 10.8 Hz, 1 H, vinyl), 2.62 (d, J = 10.8 Hz, 1 H, cyclopropyl), 1.58 (s, 3 H, CH_3), 0.13 (s, 3 H, $SiCH_3$), −0.11 (s, 3 H, $SiCH_3$); A NOE difference measurement[44] with irradiation of the methyl group led to a 15.7% increase in the vinyl proton signal and a 10.9% increase in the aromatic proton signals; MS, m/e 536.2538 (calcd for $C_{38}H_{36}OSi$, m/e 536.2535).

Anal. Calcd for $C_{38}H_{36}OSi$: C, 85.03; H, 6.76. Found: C, 84.84; H, 6.92.

Reaction of *trans*-1-Methyl-1-[(phenyldimethylsilyl)oxy]-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (27) with Tetrabutylammonium Fluoride. A solution of 32.7 mg (54.7 μmol) of *trans*-1-methyl-1-[(phenyldimethylsilyl)oxy]-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane in 25 mL of tetrahydrofuran and 61 μL (61 μmol) of a 1 M (in tetrahydrofuran) tetrabutylammonium fluoride solution was stirred for 30 min at room temperature. Workup B gave 21.8 mg of an oil whose NMR showed a 2.4:1 ratio of 5,5-diphenyl-3-(1,1-diphenylmethyl)-4-penten-2-one (**28**) to 3,3,6,6-tetraphenyl-5-hexen-2-one (**25**). The mixture was subjected to HPLC (50 × 0.95 cm silica column, 5% ether/pentane) to give the following fractions: 1, 1.0 mg of unidentified aromatic material; 2, 1.3 mg of unidentified aromatic material; 3, 5.0 mg (22.7%) of **25**, which was recrystallized with ether/pentane to yield 1.4 mg (6.4%) of very pure ketone, mp 130.5–131.5 °C (lit.[9] mp 131–133 °C); 4, 9.4 mg (42.7%) of **28**, which was recrystallized from ether/pentane to yield 4.4 mg (19.9%), mp 117–118 °C.

Reaction of *cis*-1-Methyl-1-[(phenyldimethylsilyl)oxy]-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (26) with Tetrabutylammonium Fluoride. A solution of 55.5 mg (103 μmol) of *cis*-1-methyl-1-[(phenyldimethylsilyl)oxy]-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane in 25 mL of tetrahydrofuran and 105 μL (105 μmol) of a 1 M (in tetrahydrofuran) tetrabutylammonium fluoride solution was stirred for 30 min at room temperature. Workup B gave 36.3 mg of a mixture whose NMR showed a 1.3:1 ratio of 5,5-diphenyl-3-(1,1-diphenylmethyl)-4-penten-2-one (**28**) to 3,3,6,6-tetraphenyl-5-hexen-2-one (**25**). The mixture was subjected to HPLC (50 × 0.95 cm silica column) using 5% ether/pentane to give the following fractions: 1, 1.4 mg of unidentified aromatic material; 2, 1.4 mg of unidentified aromatic material; 3, 11.8 mg (28.4%) of **25**, which was recrystallized to yield 3.5 mg (8.4%) of ketone, mp 131–132 °C (lit.[9] mp 131–133 °C); 4, 13.3 mg (32.1%) of **28**, which was purified further by recrystallization in ether/pentane to yield 4.0 mg (9.7%) of the ketone, mp 116–117.5 °C.

5,5-Diphenyl-4-penten-2-one (30).[45] To 802 mg (3.37 mmol) of 4,4-diphenyl-3-butenoic acid[46] in 30 mL of anhydrous ether at −78 °C was added 12 mL (8.52 mmol) of a 0.71 M methyllithium solution. The mixture was allowed to stir for 22.75 h and allowed to warm to room temperature. The mixture was inversely quenched by transferring the yellow solution to an ice–ammonium chloride solution mixture with a cannula. The remainder of workup A was then applied to yield 740 mg of a light brown oil, which was chromatographed on a 65 × 4 cm column slurry packed with silica gel. Elution was with 10% ether/hexane with 200-mL fractions. Fractions 7–12 contained 298 mg (37.4%) of 5,5-diphenyl-4-penten-2-one as an easily discolored oil, which solidified upon refrigeration, mp 31–34 °C. This compound was used without further purification.

Spectral data for **30**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.14–7.36 (m, 10 H, Ar), 6.28 (t, J = 7.3 Hz, 1 H, vinyl), 3.26 (d, J = 7.3 Hz, 2 H, CH_2), 2.12 (s, 3 H, CH_3); MS, m/e 236.1204 (calcd for $C_{17}H_{16}O$ m/e 236.1201).

5,5-Diphenyl-3-(1,1-diphenylmethyl)-4-penten-2-one (28). A 296 mg (2.64 mmol) portion of potassium *tert*-butoxide and 416 mg (1.75 mmol) of 5,5-diphenyl-4-penten-2-one in 30 mL of *tert*-butyl alcohol was refluxed for 10 min, and then 494 mg (2.00 mmol) of benzhydryl bromide in 25 mL of *tert*-butyl alcohol was added. The mixture was refluxed for 2.8 h and then allowed to cool. Workup A was followed by chromatography on a 48 × 3 cm column slurry packed with silica gel. Elution was with 5% ether/pentane, collecting 500-mL fractions to give the following fraction: 2, 426 mg (60.6%) of **28**, which was recrystallized from ether/hexane to yield 298 mg (42.3%) of the ketone, mp 118–119 °C.

Spectral data for **28**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.82–7.39 (m, 20 H, Ar), 5.91 (d, J = 10.3 Hz, 1 H, vinyl), 4.45 (d, J = 11.4 Hz, 1 H, benzhydryl), 4.15 (m, 1 H, CH), 1.94 (s, 3 H, CH_3); MS, m/e 402.1982 (calcd for $C_{30}H_{26}O$, m/e 402.1984).

Anal. Calcd for $C_{30}H_{26}O$: C, 89.51; H, 6.51. Found: C, 89.46; H, 6.49.

Stability of *cis*- and *trans*-1-Hydroxy-1-methyl-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (23 and 24) under Photolysis Conditions. A solution of 127 mg (315 μmol, 1.75 × 10^{-3} M) of 1,1,5,5-tetraphenyl-3-methyl-1,4-pentadien-3-ol (**3**) in 180 mL of acetonitrile was photolyzed through a Pyrex filter for 1 h with a 450-W Hanovia medium-pressure lamp. The photolysate, with 31.2 mg (188 μmol) of fluorene as an internal standard added, was concentrated under vacuum to yield 166.4 mg. NMR analysis showed 29.5 μmol of 3,3,6,6-tetraphenyl-5-hexen-2-one (**25**), 33.1 μmol of *trans*-1-hydroxy-1-methyl-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**24**), 61.2 μmol of *cis*-1-hydroxy-1-methyl-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**23**), and 164 μmol of the starting diene (91.4% mass balance). This mixture was stirred for 1.5 h in 125 mL of acetonitrile and then carefully below 45 °C under vacuum to yield 163.9 mg of material. NMR analysis showed 29.5 μmol of **25**, 33.1 μmol of **24**, 57.5 μmol of **23**, and 166 μmol of **3** (90.8% mass balance). Within experimental error the cyclopropanol did not ring-open.

Exploratory Direct Photolysis of 1,1,5,5-Tetraphenyl-3-methyl-3-[(phenyldimethylsilyl)oxy]-1,4-pentadiene (6). A solution of 158.4 mg (295 μmol, 1.55, × 10^{-3} M) of 1,1,5,5-tetraphenyl-3-methyl-3-[(phenyldimethylsilyl)oxy-1,4-pentadiene in 190 mL of acetonitrile was photolyzed for 25 min through a Corex filter with a 450-W Hanovia medium-pressure lamp. The photolysate was concentrated under vacuum to yield 166.5 mg of a yellow-green oil, whose NMR showed a 2:1.8:1 ratio of *trans*-1-methyl-1-[(phenyldimethylsilyl)oxy]-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**27**) to *cis*-1-methyl-1-[(phenyldimethylsilyl)oxy]-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**26**) to starting diene. Fractional crystallization yielded 42.4 mg (26.8%) of the cis cyclopropane, mp 166–168 °C. The filtrate was subjected to HPLC (50 × 0.95 cm silica column, 1.5% ether/pentane) to give the following fractions: 1, 53.7 mg of a mixture of the cis cyclopropane, the starting diene, and decomposition products; 2, 51.4 mg (32.5%) of the trans cyclopropane as a viscous oil pure by NMR.

General Details for Direct Quantum Yield Determination. Quantum yields were performed on the "Wisconsin black box".[10] Light output was measured by a digital actinometer[11] calibrated by ferrioxalate actinometry.[12] The two filter solution combinations used were filter A [(cell 1, 1 cm) 2.0 M nickel sulfate in 5% sulfuric

(44) Sanders, J. K. M.; Mersh, J. D. *Prog. NMR Spectrosc.* **1982**, *15*, 353–400.

(45) Cited in: Julia, M.; Schouteeten, A.; Baillarge, M. *Tetrahedron Lett.* **1974**, 3433–3434 without detail or physical properties.

(46) Johnson, W. S.; Peterson, J. W.; Schneider, W. P. *J. Am. Chem. Soc.* **1947**, *69*, 74–79.

acid, (cell 2, 1 cm) 0.8 M cobalt sulfate in 5% sulfuric acid, and (cell 3, 1 cm) 2.46×10^{-4} M bismuth trichloride in 40% hydrochloric acid (this combination gave a 32% transmission maximum at 285 nm and was opaque above 325 nm and below 250 nm)] and filter B [(cell 1, 1 cm) 2.0 M nickel sulfate in 5% sulfuric acid, (cell 2, 1 cm) 0.8 M cobalt sulfate in 5% sulfuric acid and (cell 3, 1 cm) 1.23×10^{-3} M bismuth trichloride in 40% hydrochloric acid (this combination gave a 17% transmission maximum at 280 nm and was opaque above 300 nm and below 260 nm)]. All runs used 750 mL of acetonitrile as the solvent unless otherwise noted. NMR analysis was used with fluorene as the internal standard. The quantum yields were extrapolated to 0% conversion. The estimated error is ±10% except in the case of 1,2,2,5,5-pentaphenyl-4-penten-1-one, where the error limits are ±15% due to some peak overlap in the NMR.

Summary of Direct Quantum Yield for 1,1,5,5-Tetraphenyl-3-methyl-1,4-pentadien-3-ol (3). Filter B was used. The quantum yields of formation of *cis*- and *trans*-1-hydroxy-1-methyl-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane were 0.20 and 0.19, respectively.

Summary of Direct Quantum Yield for 1,1,5,5-Tetraphenyl-3-methyl-3-[(phenyldimethylsilyl)oxy]-1,4-pentadiene (6). Filter A was used. The quantum yields of formation for *cis*- and *trans*-1-methyl-1-[(phenyldimethylsilyl)oxy]-2,2-diphenyl-3-(2,2-diphenyl-vinyl)cyclopropane were 0.22 and 0.34, respectively.

Summary of Direct Quantum Yields for 1,1,3,5,5-Pentaphenyl-1,4-pentadien-3-ol (4). Filter B was used. The quantum yields of formation of *cis*- and *trans*-1-hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane were 0.24 and 0.067, respectively.

Summary of Direct Quantum Yields for 1,1,3,5,5-Pentaphenyl-3-[(phenyldimethylsilyl)oxy]-1,4-pentadiene (7). Filter A was used. The quantum yields of formation of *cis*- and *trans*-1,2,2-triphenyl-1-[(phenyldimethylsilyl)oxy]-3-(2,2-diphenylvinyl)cyclopropane were 0.16 and 0.12, respectively.

Summary of Direct Quantum Yield Results for 1,1,3,3-Tetraphenyl-2-propen-1-ol (2). All runs were in 750 mL of *tert*-butyl alcohol. Filter A was used. The quantum yield was determined to be 0.0071.

Summary of Direct Quantum Yields for 1,1,3,3-Tetraphenyl-2-propen-1-ol (2) in Acetonitrile. Filter A was used. The quantum yield of formation for *cis*-1,2,2,3-tetraphenylcyclopropan-1-ol was 0.024.

Summary of Direct Quantum Yield for 1,2,2,5,5-Pentaphenyl-4-penten-1-one (18). Filter A was used. The quantum yields of formation for *cis*- and *trans*-1-hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane were 0.0040 and 0.0044, respectively.

General Details for Triplet Quantum Yields Determination. Triplet quantum yields were performed on the semimicro-optical bench.[10] Light output was measured by a digital actinometer[11] calibrated by ferrioxalate actinometry.[12] For the microbench runs, the monochromator entrance slit was set at 5.4 mm and the exit slit at 3.0 mm, to give a band pass of 22 nm at half-peak height. All runs were done at 334 nm in 50 mL of acetonitrile, and 200-MHz NMR analysis was used with fluorene as the internal standard. All runs were extrapolated to 0% conversion.

Summary of the Triplet Quantum Yield Run for 1,1,5,5-Tetraphenyl-3-methyl-1,4-pentadien-3-ol (3). Part of the xanthone was crystallized from the photolysate with ether/pentane prior to analysis. The amount of light absorbed was 9.65×10^{-2} mE and no reaction was observed. The quantum yield of formation for each of the cyclopropanols was less than 0.025.

Summary of the Triplet Quantum Yield Run for 1,1,5,5-Tetraphenyl-3-[(phenyldimethylsilyl)oxy]-3-methyl-1,4-pentadiene (6). The amount of light absorbed was 1.08×10^{-1} mE, and no reaction was observed. The quantum yield for formation for each of the cyclopropanes was less than 0.02.

Summary of Triplet Quantum Yield Runs for 1,1,3,5,5-Pentaphenyl-1,4-pentadien-3-ol (4). Part of the xanthone was crystallized from the photolysate with ether/pentane prior to analysis. The quantum yields of formation of *cis*- and *trans*-1-hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane were 0.47 and 0.049, respectively.

Summary of Triplet Quantum Yield Runs for 1,1,3,5,5-Pentaphenyl-3-[(phenyldimethylsilyl)oxy]-1,4-pentadiene (7). The quantum yields of formation of *cis*- and *trans*-1,2,2-triphenyl-1-[(phenyldimethylsilyl)oxy]-3-(2,2-diphenylvinyl)-cyclopropane were 0.49 and 0.090, respectively.

Exploratory Direct Photolysis of *cis*-1-Hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane (14). A solution of 148.1 mg (319 μmol, 1.39×10^{-3} M) of **14** in 230 mL of acetonitrile was photolyzed for 2.3 h through a Pyrex filter with a 450-W Hanovia medium-pressure lamp. The photolysate was concentrated under vacuum to yield 157.5 mg of a viscous oil whose NMR spectrum revealed a 23:8:1 ratio of **14** to *trans*-1-hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane (**15**) to 1,2,2,5,5-pentaphenyl-4-penten-1-one (**18**). The mixture was subjected to HPLC (50 × 0.95 cm silica column, 15% ether/pentane) to give the following fractions: 1, 11.1 mg (9.72%) of impure 1,1,4,4-tetraphenyl-1,3-butadiene, which was recrystallized from ether/pentane to yield 4.3 mg (3.8%) of compound, mp 195–197 °C (lit.[39] mp 200 °C), pure by NMR; 2, 11.8 mg of unidentified aromatic compounds; 3, 12.0 mg of a mixture of compounds that included **18**; 4, 56.2 mg (38.0%) of **14**; 5, 22.0 mg (14.9%) of **15**. Fraction 3 was rechromatographed (4% ether/pentane) to give 4.8 mg (3.28%) of slightly impure 1,2,2,5,5-pentaphenyl-4-penten-1-one. Recrystallization from ether/pentane yielded 1.9 mg (1.3%) of the ketone, mp 169–171 °C.

Exploratory Sensitized Photolysis of *cis*-1-Hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane (14). A solution of 150.4 mg (324 μmol, 1.71×10^{-3} M) of **14** and 87.6 mg (389 μmol, 2.04×10^{-3} M) of 4-(*N*,*N*-dimethylamino)benzophenone in 190 mL of acetonitrile was photolyzed through a Pyrex filter with a 1.4×10^{-2} M sodium metavanadate solution circulating through the cooling jacket for 1.67 h with a 450-W Hanovia medium-pressure lamp. The photolysate was concentrated under vacuum to yield 239.5 mg of a mixture which included a 10:7.6:1 ratio of **14** to *trans*-1-hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane (**15**) to 1,2,2,5,5-pentaphenyl-4-penten-1-one (**18**) by NMR. The mixture was subjected to HPLC (8 × 0.95 cm silica precolumn in series with a 50 × 0.95 cm silica column, 30% ether/pentane) to give the following fractions: 1, 10.0 mg (8.6%) of 1,1,4,4-tetraphenyl-1,3-butadiene (**22**), mp 189–196 °C, which was recrystallized from ether/pentane to give 5.7 mg (4.9%) of the butadiene, mp 198–200 °C (lit.[39] mp 200 °C); 2, of 70.0 mg of a mixture of compounds that included **14** and **18**; 3, 33.3 mg (22%) of **15**; 4, 10.9 mg of unidentified aromatic material; 5, 85.2 mg (378 μmol) of 4-(*N*,*N*-dimethylamino)benzophenone. Fraction 2 was rechromatographed twice more (50 × 0.95 cm silica column, 15%, 4% ether/pentane) to give 32.5 mg (21.6%) of **14** and 2.5 mg (1.7%) of impure **18**, which was recrystallized from ether/pentane to yield 2.3 mg (1.5%) of the ketone, mp 172–173 °C.

Exploratory Direct Photolysis of *cis*-1,2,2-Triphenyl-1-[(phenyldimethylsilyl)oxy]-3-(2,2-diphenylvinyl)cyclopropane (16). A solution of 61.7 mg (103 μmol, 5.42×10^{-4} M) of **16** in 190 mL of acetonitrile was photolyzed for 57 min through a Pyrex filter with a 450-W Hanovia medium-pressure lamp. The photolysate was concentrated to yield 66.3 mg of a viscous oil whose NMR showed a 2.2:1 ratio of **16** to the trans isomer **17**. Crystallization from ether of the photolysate gave 12.6 mg (20.5%) of a 1.3:1 mixture of cis to trans cyclopropane in this case. The filtrate was subjected to HPLC (50 × 0.95 cm silica column, 1.5% ether/pentane) to give the following fractions: 1, 37.8 mg (61.4%) of **16** as a waxy solid slightly contaminated with the trans isomer, which was recrystallized from ether/pentane to yield 15.2 mg (24.7%) of the cis cyclopropane, mp 170–171.5 °C; 2, 10.6 mg (17.2%) of **17**, mp 171–175 °C, which was recrystallized to yield 4.4 mg (7.1%) of the cyclopropane, mp 179–182 °C.

Exploratory Direct Photolysis of *trans*-1,2,2-Triphenyl-1-[(phenyldimethylsilyl)oxy]-3-(2,2-diphenylvinyl)cyclopropane (17). A solution of 87.1 mg (146 μmol, 7.68×10^{-4} M) of **17** in 190 mL of acetonitrile was photolyzed for 1.33 h through a Pyrex filter with a 450-W Hanovia medium-pressure lamp. The photolysate was concentrated under vacuum to yield 101.9 mg of an oil whose NMR showed a 1.8:1 ratio of **17** to **16**. Fractional cyrstallization from ether gave 43.4 mg (49.7%) of the trans cyclopropane slightly contaminated with the cis isomer, mp 169–174 °C. The filtrate was subjected to HPLC (50 × 0.95 cm HPLC silica column, 1.5% ether/pentane) to give the following

fractions: 1, 28.0 mg (32.1%) **16**, mp 153–157 °C, contaminated by the trans cyclopropane, which was recrystallized from ether/pentane to yield 14.4 mg (16.5%) of cis cyclopropane, mp 171–173 °C; 2, 9.7 mg (10.5%) of the transcyclopropane, mp 164–174 °C. This fraction was combined with the solid from the fractional crystallization and recrystallized from ether/pentane to yield 41.4 mg (47.4%) of **17**, mp 179–182 °C.

Exploratory Sensitized Photochemistry of *trans*-1,2,2-Triphenyl-1-[(phenyldimethylsilyl)oxy]-3-(2,2-diphenylvinyl)cyclopropane (17). A solution of 50.5 mg (84.4 μmol, 4.69×10^{-4}) of **17** and 57.5 mg (293 μmol, 1.54×10^{-3} M) of xanthone in 180 mL of acetonitrile was photolyzed for 31 min through a Pyrex filter and a 2.0×10^{-2} M sodium metavanadate solution circulating through the cooling jacket of a 450-W Hanovia medium-pressure lamp. The photolysate was concentrated under vacuum to yield 111.4 mg of a mixture of sensitizer and vinylcyclopropanes. The NMR showed a 2.25:1 ratio of **17** to **16**. The mixture was subjected to a HPLC (50 × 0.95 cm silica column, 25% ether/pentane) to give fractions A1, 42.7 mg (84.6%) of the vinylcyclopropanes, and A2, 48.5 mg (247 μmol) of xanthone. Fraction A1 was fractionally crystallized to give 13.8 mg (27.4%) of **17** contaminated with the cis isomer. The filtrate was subjected to HPLC (1.5% ether/pentane to give the following) fractions: B1, 7.4 mg (14.7%) of the cis cyclopropane with a trace of the trans isomer present; B2, 19.0 mg (37.7%) of the trans cyclopropane, mp 178–180 °C. Fraction B2 and the solid that was fractionally crystallized were recrystallized from ether/pentane to yield 29.1 mg (57.6%) of trans cyclopropane, mp 179–180 °C.

Exploratory Direct Photolysis of 1,2,2,5,5-Pentaphenyl-4-penten-1-one (18). A solution of 94.1 mg (202 μmol, 1.12×10^{-3} M) of 1,2,2,5,5-pentaphenyl-4-penten-1-one in 180 mL of acetonitrile was photolyzed for 1 h 34 min through a Pyrex filter with a 450-W Hanovia medium-pressure lamp. The photolysate was concentrated under vacuum to yield 102.4 mg of a mixture whose NMR showed a 5.6:5.6:1 ratio of *cis*-1-hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane (**14**) to *trans*-1-hydroxy-1,2,2-triphenyl-3-(2,2-diphenylvinyl)cyclopropane (**15**) to 1,2,2,5,5-pentaphenyl-4-penten-1-one (**18**). The mixture was subjected to HPLC (50 × 0.95 cm silica column, 15% ether/pentane) to give the following fractions: A1, 11.6 mg (16.0%) of impure 1,1,4,4-tetraphenyl-1,3-butadiene (**22**), which was recrystallized from ether/pentane to yield 7.0 mg (9.65%) of **22**, mp 196–199 °C (lit.[39] mp 200 °C); A2, 8.4 mg of unidentified aromatic material; A3, 16.2 mg of a mixture of compounds including the starting ketone; A4, 19.7 mg (21.0%) of **14**; A5, 15.8 mg (16.8%) of **15**. Fraction A3 was subjected to HPLC (4% ether/pentane) to give 6.2 mg (6.58%) of slightly impure **18**, which was recrystallized from ether/pentane to yield 4.2 mg (9.0 μmol, 4.56%) of the ketone, mp 169–171 °C.

Single Photon Counting. The apparatus and procedure have been described previously.[13a] The solvents were methylcyclohexane (Kodak Spectral Grade) and isopentane purified as described previously.[13a] Individual samples were prepared in a 4:1 methylcyclohexane–isopentane solution to give an optical density in the range 0.80–1.5, thoroughly degassed by at least four freeze–thaw cycles immediately before counting, and counted at 77 K until a minimum of 1500 counts in the maximum channel (512 channels total) were obtained. Data were collected at less than 5% of the 30–40-kHz lamp flash rate to ensure exclusion of double photon counting. In separate runs excitation was varied over the range 265–275 nm, and emission was monitored over the range 300–315 nm with an RCA 8850 photomultiplier. The decay rate was independent of excitation and emission wavelengths employed. A single exponential decay function was found in all cases. The data are reported as follows: lifetime at 77 K, 2.6 ns; lifetime at room temperature, 74 ps; rate of decay at 77 K, 3.8×10^8 s^{-1}; rate of decay at room temperature, 1.33×10^{10}; rate of reaction at room temperature, 9.31×10^7; number of runs, 4; and an estimated 10% error in rate.

Fluorescence Studies.[13a] The fluorescence spectrum was recorded in 4:1 methylcyclohexane–isopentane solution at 77 and 295 K under otherwise identical conditions. Details are given in the supplementary material.

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Supplementary Material Available: Crystal data, positional parameters, interatomic distances, bond angles, anisotropic and isotropic temperature factors, and an ORTEP drawing for *cis*-1,2,2-triphenyl-1-[(phenyldimethylsilyl)oxy]-3-(2,2-diphenylvinyl)cyclopropane, general experimental information, and IR data for **3–9**, **11**, **13–20**, and **26–28** (13 pages). Ordering information is given on any current masthead page.

Synthesis of Benzhydryl 2α-(Chloromethyl)-2β-methyl-6,6-dihydropenam-3α-carboxylate 1,1-Dioxide: The 2α-Isomer of the Potent β-Lactamase Inhibitor BL-P2013

Samarendra N. Maiti,† Paul Spevak,† Kazuo Ogawa,‡ and Ronald G. Micetich*,†

SynPhar Laboratories Inc., 4290 91A St., Edmonton, Alberta, Canada T6E 5V2, and Taiho Pharmaceutical Co., Ltd., Tokushima, Japan

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In order to study the effect of stereochemical changes on the activity of an active group of β-lactamase inhibitors, the 2β-(substituted methyl)penam 1,1-dioxides, an investigation of the method for the preparation of 2α-(substituted methyl)penam was undertaken. The described 2α-(chloromethyl)penam 1β-sulfoxide **11** was conveniently obtained by the thermolytic rearrangement of the 2β-(chloromethyl)penam 1α-sulfoxide **10**. The preparation and β-lactamase inhibitory activity of the 2α-isomer of the active β-lactamase inhibitor BL-P2013 are reported.

The introduction of benzylpenicillin into clinical practice about 45 years ago was almost immediately followed by the discovery of resistant strains of pathogenic microorganisms. One of the major causes of bacterial resistance to the β-lactam antibiotics is the ability of these bacteria to produce β-lactamases that catalyze the hydrolysis of the β-lactam antibiotics to the inactive penicilloic acids. The

† SynPhar Laboratories Inc.
‡ Taiho Pharmaceutical Co., Ltd.

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