a Rh(III)–H(terminal) bond should be about 1.70 Å in length. This is consistent with available information, *viz.*, Rh(I)–H = 1.60 (12) Å in $HRh(CO)[P(C_6H_5)_3]_3$,[32] and Rh(III)–H = 1.48 (esd unspecified, but large) in $HRhCl(SiCl_3)[P(C_6H_5)_3]_2$.[33]

Our present value of Rh–H = Rh′–H = 1.849 (47) Å seems to be significantly greater than for terminal Rh–H bonds, although the estimated standard deviation is high. This result is expected and is in agreement with information available on diborane where terminal hydride ligands (H_t) are significantly closer to boron than the bridging ligands (H_b). [X-Ray diffraction results are B–B = 1.762 (10), B–H_t = 1.06 (2) and 1.09 (2), and B–H_b = 1.24 (2) and 1.25 (2) Å;[34] electron diffraction results are B–B = 1.775 (3), B–H_t = 1.196 (+0.008, −0.006), and B–H_b = 1.339 (+0.002, −0.006) Å;[35] spectroscopic results are B–B = 1.770 (5), B–H_t = 1.192 (10), and B–H_b = 1.329 (5) Å.[36]]

Finally we may note that positions of bridging hydride ligands determined from X-ray diffraction studies are not so prone to systematic errors as those of terminal hydride ligands since the deviations of the electron density from spherical symmetry in the former case act such as to conserve the same center of gravity (save for a small displacement perpendicular to the metal–metal vector).

Acknowledgments. This work was made possible by computing time donated by the Computer Center, University of Illinois at Chicago Circle, and by a grant from the National Science Foundation (GP-33018, to M. R. C.). We thank Professor P. M. Maitlis for the sample studied and Dr. B. G. DeBoer for assistance with computational problems.

(32) S. J. LaPlaca and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).

(33) K. W. Muir and J. A. Ibers, *Inorg. Chem.*, **9**, 440 (1970).

(34) D. S. Jones and W. N. Lipscomb, *Acta Crystallogr., Sect. A*, **26**, 196 (1970).

(35) L. S. Bartell and B. L. Carroll, *J. Chem. Phys.*, **42**, 1135 (1965).

(36) K. Kuchitscu, *ibid.*, **49**, 4456 (1968).

Accentuation of Di-π-methane Reactivity by Central Carbon Substitution. Mechanistic and Exploratory Organic Photochemistry. LXXV[1]

Howard E. Zimmerman,* Robert J. Boettcher, and Werner Braig

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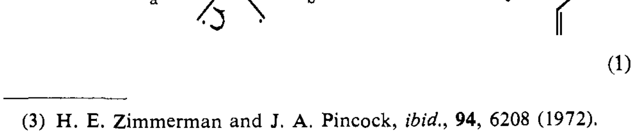
Abstract: The photochemistry of 1,1,3,3-tetraphenyl-5-methyl-1,4-hexadiene was investigated to ascertain the effect of central phenyl substitution on the di-π-methane rearrangement. The synthesis of this tetraphenyl diene is described. The tetraphenyl diene was found to afford two products on direct irradiation, 1,1,2,2-tetraphenyl-3-(2-methylpropenyl)cyclopropane and 1,1,2,3-tetraphenyl-2-(2-methylpropenyl)cyclopropane. The first of these arises from the usual di-π-methane mechanism with vinyl–vinyl bonding as the initial excited state process. The second product results from phenyl–vinyl interaction. Phenyl–vinyl bridging selectively involves the vinyl group with the lower energy singlet excitation. The product structures were elucidated by nmr, mass spectral analysis, and degradation. The quantum efficiency on direct irradiation was determined as Φ = 0.076 for the 1,1,2,2-cyclopropane and Φ = 0.051 for the 1,1,2,3-cyclopropane. Sensitization with acetophenone gave none of the 1,1,2,3-cyclopropane but afforded the 1,1,2,2-cyclopropane much more efficiently, with a quantum yield of Φ = 0.42. Additionally, the sensitized runs yielded some 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene, a product resulting from a new type of photochemical rearrangement. This was formed with an efficiency of Φ = 0.010. Thus, in the present di-π-methane system the triplet was quite reactive in contrast to previous acyclic cases. This is understood as a consequence of central phenyl substitution affecting the reactivity of a vinyl–vinyl bridged species along the reaction coordinate. An additional factor is inhibited energy dissipation as a result of steric hindrance preventing facile twisting of the excited vinyl groups. In the course of the research, a simple preparation of a high surface area support for efficient high-speed, high-pressure liquid chromatography was developed.

Previous extensive studies of the di-π-methane rearrangement[2] have focused attention both on cyclic and acyclic examples and established the very broad generality of the reaction. In most of the acyclic examples studied, there has been central methyl substitution on the methane carbon (*i.e.*, R = CH_3 in eq 1). It has been demonstrated[3] that the di-π-methane process is inefficient without such substitution. This was interpreted in terms of the need for odd-electron stabilization in the ring opening step b of eq 1.



(1)

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[1] For the previous paper of this series note: H. E. Zimmerman and M.-L. Viriot-Villaume, *J. Amer. Chem. Soc.*, **95**, 1274 (1973).

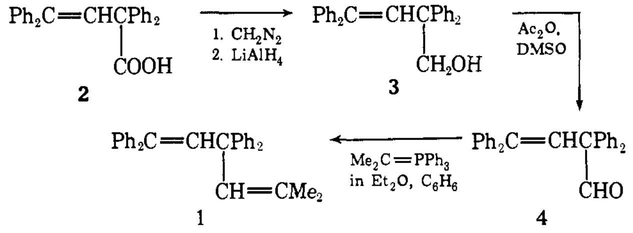
[2] (a) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969); (b) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6259 (1970); (c) *ibid.*, **92**, 6267 (1970); (d) H. E. Zimmerman and A. A. Baum, *ibid.*, **93**, 3646 (1971); (e) H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. Kurtz, *ibid.*, **94**, 5504 (1972); (f) H. E. Zimmerman and G. Epling, *ibid.*, **94**, 8749 (1972); (g) H. E. Zimmerman and G. E. Samuelson, *ibid.*, **91**, 5307 (1969); (h) P. S. Mariano and J. Ko, *ibid.*, **94**, 1766 (1972).

[3] H. E. Zimmerman and J. A. Pincock, *ibid.*, **94**, 6208 (1972).

It therefore seemed of considerable interest to study the di-π-methane rearrangement where the central substituents were phenyl and where the ring-opening step might therefore be further enhanced. The compound chosen for study was 1,1,3,3-tetraphenyl-5-methyl-1,4-hexadiene (**1**).

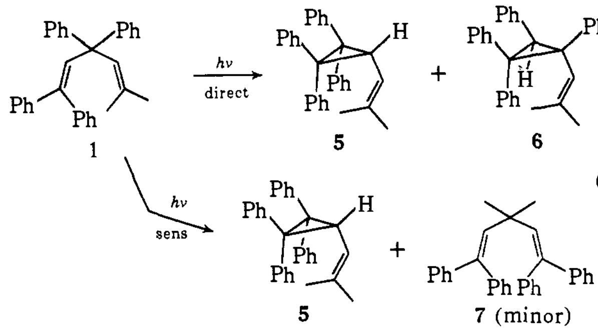
Synthesis of Reactant. A convenient starting material was 2,2,4,4-tetraphenyl-3-butenoic acid (**2**) described by Schlenk and Bergmann.[4] The corresponding methyl ester was reduced with lithium aluminum hydride to the carbinol **3**, which, in turn, was efficiently oxidized by the Albright–Goldman procedure[5] to aldehyde **4**. Reaction of this aldehyde with isopropylidenetriphenylphosphorane in ether–benzene afforded the desired 1,1,3,3-tetraphenyl-5-methyl-1,4-hexadiene (**1**). The synthesis is outlined in Chart I.

Chart I. Synthesis of 1,1,3,3-Tetraphenyl-5-methyl-1,4-hexadiene



Exploratory Photolyses and Product Separation. Direct irradiation was carried out using a 450-W immersion apparatus and a glass filter cutting off below 260 nm.[6] In a 50% conversion run, a 60% yield (based on unrecovered reactant) of two cyclopropane products was obtained. The principal loss of material was derived from secondary reaction of the cyclopropane products. Traditional silica gel chromatography nicely separated photochemical reactant **1** from the reaction mixture. Ethanol–methylene chloride recrystallization of the product fraction allowed isolation of the major photochemical product **5**, mp 143.5–144.5°. With considerably more difficulty, the second photochemical product **6**, mp 136–137°, was obtained. However, the separation and purification of these products were far from ideal, and it was clear that an improved mode of separation was needed.

Acetophenone-sensitized photolysis proved to be much less complex and afforded primarily the mp 143.5–144.5° product **5** observed in the direct runs. Additionally, evidence was obtained for the formation of *ca.* 2% of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene[2a] (**7**). The evidence for the presence of this product was the appearance of a peak with the correct retention time or volume on two different vpc columns and on analytical high-pressure liquid chromatography. These results are formulated in eq 2.



(2)

Product Separation, Product Analysis, and Development of an Efficient High-Pressure Liquid Chromatographic Packing. It was apparent from the silica gel column chromatography results (*vide supra*) and other attempted chromatographic separation attempts that some more efficient method was required. High-pressure, high-speed liquid chromatography is a relatively new method[8] which promised to be of value. One of the most efficient approaches seems to be use of a 20–50-μ glass bead material coated with a thin film of permanently bonded stationary phase. Unfortunately, experimental details for preparation of these packings seem lacking in the chemical literature and the amounts required for preparative purposes are unavailable.[8c,d] In view of these limitations, we developed a suitable packing which proved useful in the present research and which should be of general value. The procedure involved generating silicate functional groups on the surface of glass microbeads by refluxing with sodium hydroxide, and then reacting this surface with silicon tetrachloride or octadecyltrichlorosilane and subsequently hydrolyzing (see Experimental Section for details).

Using a $^3/_8$ in. × 12 ft column, it proved possible to separate starting material and each of the photoproducts. Injections of 65 mg per scan did not overload the column. Analytical runs could be completed in 1.5 hr and preparative runs required only about 2 hr. Hence the method is exceedingly useful for preparative and analytical[9] use; further description is to be found in the Experimental Section.

Using this approach to product separation, it was ascertained that the photoproduct mixture in direct irradiations consisted of just the two compounds **5** and **6** in a *ca.* 3:2 ratio. The method also was used to obtain the two photoproducts in sufficient quantity for degradation and structure elucidation.

Photoproduct Structure Elucidations. The structure of the major photoproduct **5**, mp 143.5–144.5°, was initially suggested by the nmr spectrum which revealed the presence of two nonequivalent methyl groups (τ 7.96 and 8.21), a single vinyl hydrogen (τ 4.96, J = 9.5 Hz) coupled to a single methine hydrogen (τ 6.49, J = 9.5 Hz), and a complex aromatic absorption (τ 2.6–3.4) integrating for 20 hydrogens. Rigorous confirmation of the structure was derived from degradation, which is outlined in Chart II. Oxidation of the mp 143.5–144.5° photoproduct **5** by the method of von Rudloff[10] gave primarily 2,2,3,3-tetraphenylcyclopropanecarboxylic acid (**8**) and acetone, plus some

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[4] W. Schlenk and E. Bergmann, *Justus Liebigs Ann. Chem.*, **463**, 228 (1928).

[5] J. D. Albright and L. Goldman, *J. Amer. Chem. Soc.*, **89**, 2416 (1967).

[6] A Corex filter was used but checked spectrophotometrically in view of the report of Morrison[7] that Corex produced presently no longer efficiently cuts off below 260 nm.

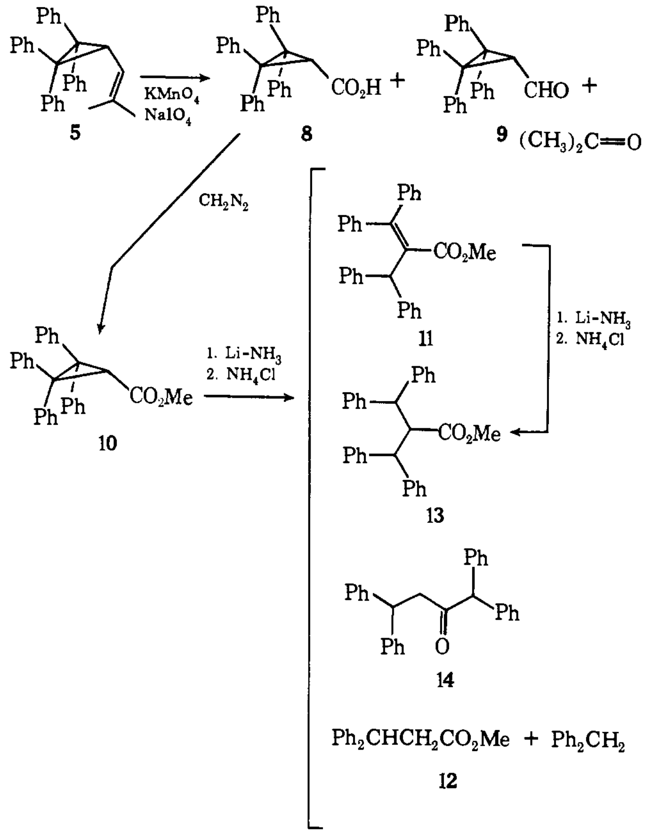
[7] H. Morrison, private communication.

[8] (a) For a review of the method, see J. J. Kirkland, "Modern Practice of Liquid Chromatography," Wiley-Interscience, New York, N. Y., 1971. (b) Note also J. J. Kirkland, *Anal. Chem.*, **43**, 36A (1971). (c) One commercial product, Zipax,[8e] is available in limited amounts and seems to have too low a capacity (note ref 8b) for preparative work. (d) The preparation of a second commercial product, Corasil (Waters Co.), has not been detailed in the literature and the product is available in limited quantities. (e) J. J. Kirkland (Du Pont) U. S. Patent 3,488,-922 (1970); *Chem. Abstr.*, **72**, P70984 (1970).

[9] For analytical use commercial columns proved satisfactory as well.

[10] E. von Rudloff, *Can. J. Chem.*, **33**, 1714 (1955).

Chart II. Degradation of the Major Photoproduct



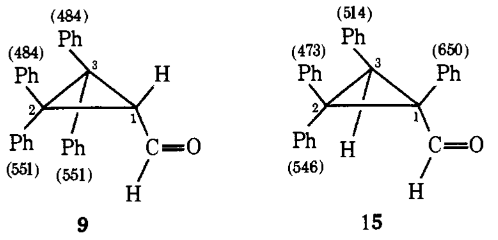


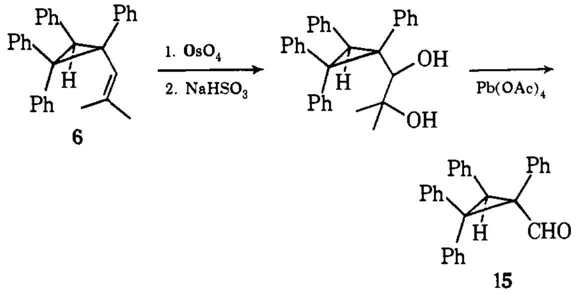
Figure 1. Chemical shifts of ortho hydrogens with Eu(fod)$_3$: Hz downfield from TMS for mole ratio of 1.12, Eu(fod)$_3$ to aldehyde, where the aldehyde is essentially completely complexed.[13]

2,2,3,3-tetraphenylcyclopropanecarboxaldehyde (**9**). Lithium–liquid ammonia reduction of the corresponding methyl ester **10** gave as major products methyl 3,3-diphenyl-2-(diphenylmethyl)-2-propenoate (**11**) and 3,3-diphenylpropionate (**12**), and diphenylmethane. Additionally, there was nmr evidence for the formation of methyl dibenzhydrylacetate (**13**) and 1,1,4,4-tetraphenyl-2-butanone (**14**). The 3,3-diphenyl-2-(diphenylmethyl)-2-propenoate (**11**) was then reduced with lithium–liquid ammonia to give methyl dibenzhydrylacetate, whose corresponding acid is known.[11]

Turning now to the minor photoproduct **6**, we noted the similarity of the ultraviolet spectrum with that of the vinylcyclopropane major product **5**. Thus, the maximum at 228 nm (ϵ 29,300) and shoulders at 267 (1630) and 274 (914) compared well with the peaks at 225 nm (ϵ 27,400), 269 (1820), and 275 (1005) given by vinylcyclopropane **5**.

That a vinylcyclopropane structure was indeed correct was evidenced by the nmr of the minor photoproduct **6** which revealed only a single nonvinyl, nonaromatic hydrogen together with a single vinyl hydrogen. The vinyl hydrogen peak at τ 3.88 was slightly coupled (J = 1.0 Hz) to two methyl absorptions observed at τ 8.47 and 9.24; this indicated the presence of an isopropylidene moiety. The absence of any coupling of this vinyl hydrogen, except with the methyls, indicated that the vinyl was substituted on a quaternary ring carbon. This was in agreement with the observation of a single uncoupled methine peak at τ 6.06. The balance of the hydrogens appeared in the aromatic region of the nmr (*i.e.*, 20 hydrogens at τ 2.60–3.20).

This evidence uniquely supports 1,1,2,3-tetraphenyl-2-(2-methylpropenyl)cyclopropane as the structure of **6**. Further support was derived from the oxidative cleavage of **6** with osmium tetroxide followed by lead tetraacetate, which afforded aldehyde **15**. The infrared of the carbonyl was found at 5.93 μ, characteristic of a cyclopropyl aldehyde.[2a,12]



(3)

Still further information was derived from the effect of tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium(III)[13] on the nmr spectrum of aldehyde **15**. The europium reagent revealed two ortho hydrogens for each of four differently located phenyl groups. As expected for structure **15**, the ortho hydrogens for one phenyl group (at C-1 in Figure 1) were shifted very far downfield (*i.e.*, to 650 Hz). A second phenyl had its hydrogens shifted quite similarly (*i.e.*, to 546 *vs.* 551 Hz) to the shift observed for the cis phenyls of aldehyde **9** derived from the major photoproduct **5**. This suggests that only one phenyl is cis in aldehyde **15**. Furthermore, the shifts observed with europium for aldehyde **15** generally paralleled those expected from the behavior of the nmr spectrum of **9**. This is illustrated in Figure 1. The relatively low field for the phenyl at C-3 compared with the model compound **9** is readily understood by its greater accessibility as a result of lack of steric blocking by a cis phenyl at this carbon and by a preferred conformation in which the lanthanide complexed carbonyl oxygen is aimed in this direction.

Final definitive proof of the structure of minor photoproduct **6** derived from the degradation of aldehyde **15** is delineated in Chart III. Thermolysis of aldehyde **15** in refluxing xylene for 2 hr gave a quantitative yield of 3,4,5,5-tetraphenyldihydrofuran (**16**). This cleaved into the keto formate **17** on treatment with osmium tetroxide and sodium bisulfite, followed by lead tetraacetate. The keto formate nicely deformylated to give the β-hydroxy ketone **18** which reverse aldolized

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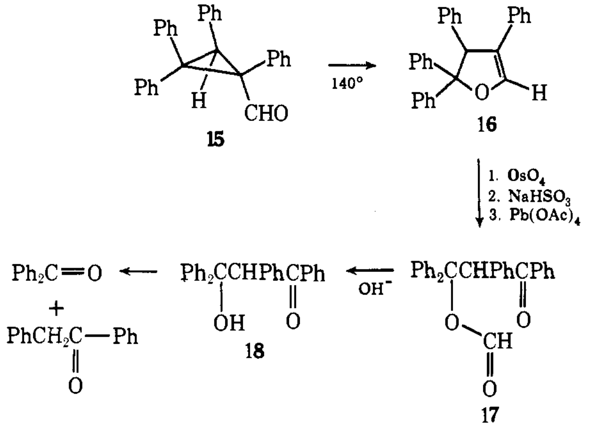
(11) A. C. Cope and W. R. Lyman, *J. Amer. Chem. Soc.*, **75**, 3312 (1953).

(12) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962.

(13) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, **93**, 1522 (1971).

Chart III. Degradation of Minor Photoproduct **6**



under the basic reaction conditions to give benzophenone and desoxybenzoin.

Determination of Quantum Yields and Reaction Multiplicity. Results. For this portion of the research, the Wisconsin Black Box[14] was used. A 245–312-nm solution filter was used in direct irradiations and a 295–360-nm filter was used in sensitized runs. For sensitization, an acetophenone energy donor was used since its 74 kcal/mol energy seemed sufficient in view of the expected triplet excitation energy of 62 kcal/mol for a styryl moiety[15] as present in the tetraphenyl diene reactant **1**. The results are listed in Table I. To avoid secondary photolysis, runs were made at various conversions ranging down to 6%. In the sensitized runs, concentrations were adjusted so that acetophenone singlets would decay to the triplets before collision with the acceptor, but triplet energy transfer would be efficient.[16] Also the wavelength of irradiation was selected so that greater than 99% of the light was captured by the acetophenone sensitizer.

Table I. Quantum Yield Determination for Photolysis of 1,1,3,3-Tetraphenyl-5-methyl-1,4-hexadiene (**1**)

Run	[1], M[b]	Sensitizer (M)[c]	Conv, %	Quantum yields[a] Φ_5	Φ_6	Φ_7
1	0.002		43	0.070	0.045	<0.0002
2	0.002		28	0.074	0.044	<0.0002
3	0.002		6	0.076	0.051	d
4	0.002	Acetophenone (0.31)	55	0.25		0.006
5	0.002	Acetophenone (0.31)	19	0.42		0.01

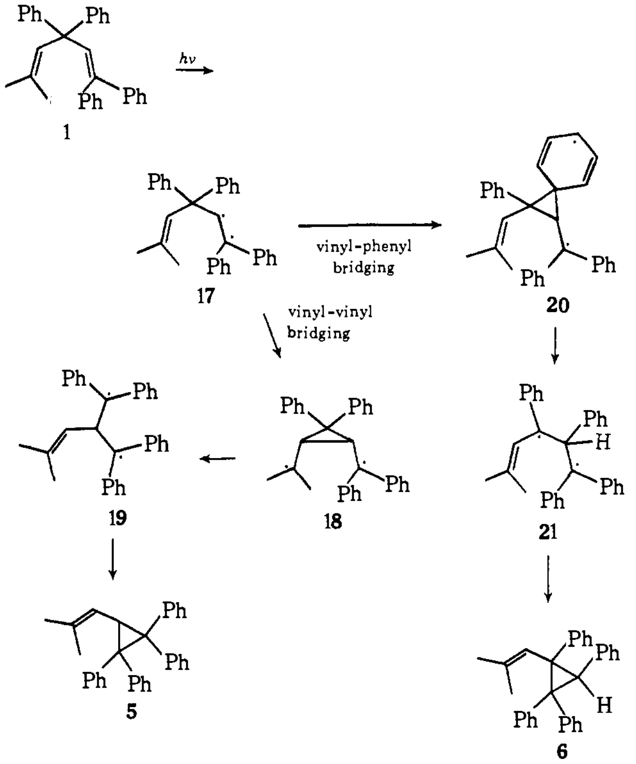
[a] Φ_5 refers to efficiency of formation of 1,1,2,2-tetraphenyl-3-(2-methylpropenyl)cyclopropane, Φ_6 refers to efficiency of formation of 1,1,2,3-tetraphenyl-2-(2-methylpropenyl)cyclopropane, and Φ_7 refers to efficiency of formation of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene. [b] *tert*-Butyl alcohol solvent. [c] >99% of the light absorbed by sensitizer. [d] Not determined.

The analyses were carried out by analytical high-pressure liquid chromatography on $^1/_8$ in. × 6 ft of Corasil/C18 eluted with 58% acetonitrile–water at 0.6 ml/min, using uv optical density areas. An internal standard (1,4-diphenyl-1,3-butadiene) and calibration with known mixtures of the photoproducts and reactant were used.

Additionally, direct photolyses were run in *tert*-butyl alcohol with increasing concentrations of 1,3-cyclooctadiene. In these runs the ratio of the two major photoproducts **5** and **6** were determined. However, even at 1.89 M quencher there was no significant change in this ratio detected (see Experimental Section).

Interpretative Discussion. Gross Mechanisms of Rearrangement. The formation of two products, 1,1,2,2-tetraphenyl-3-(2-methylpropenyl)cyclopropane (**5**) and 1,1,2,3-tetraphenyl-2-(2-methylpropenyl)cyclopropane (**6**) as observed in the direct irradiations, can be ascribed to competitive vinyl–vinyl bridging *vs.* phenyl–vinyl bridging. Both mechanisms have precedent[17] and are outlined in Chart IV.

Chart IV. Gross Mechanisms of Formation of the Isomeric Cyclopropane Products **5** and **6**



We note regiospecificity in the reaction of the vinyl–vinyl bridged species **18**, and this indeed does have precedent in our earlier studies.[2b,c] This seems most likely to arise from the mechanistic driving force cited in these earlier studies; this relates to the fact that benzhydryl delocalization energy is retained in the unzip-

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(14) H. E. Zimmerman, *Mol. Photochem.*, **3**, 281 (1971).

(15) (a) D. F. Evans, *J. Chem. Soc.*, 1351 (1957); (b) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(16) Diene concentrations of 2 × 10^{-3} M were used. Assuming singlet energy transfer to be diffusion controlled with a rate constant of the order of 10^9 l. mol^{-1} sec^{-1}, the pseudo-unimolecular rate of singlet excitation transfer becomes *ca.* 10^6 sec^{-1}. Allowing an order of magnitude margin of error, at most 0.1% of the acetophenone singlets would be capable of energy transfer. See also H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **89**, 906 (1967), ref 8–10.

(17) For vinyl–vinyl bridging processes note ref 2a–e, 2h, and 18. For vinyl–aryl bridging, note ref 2f–g, 19, and 20a and b.

(18) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966).

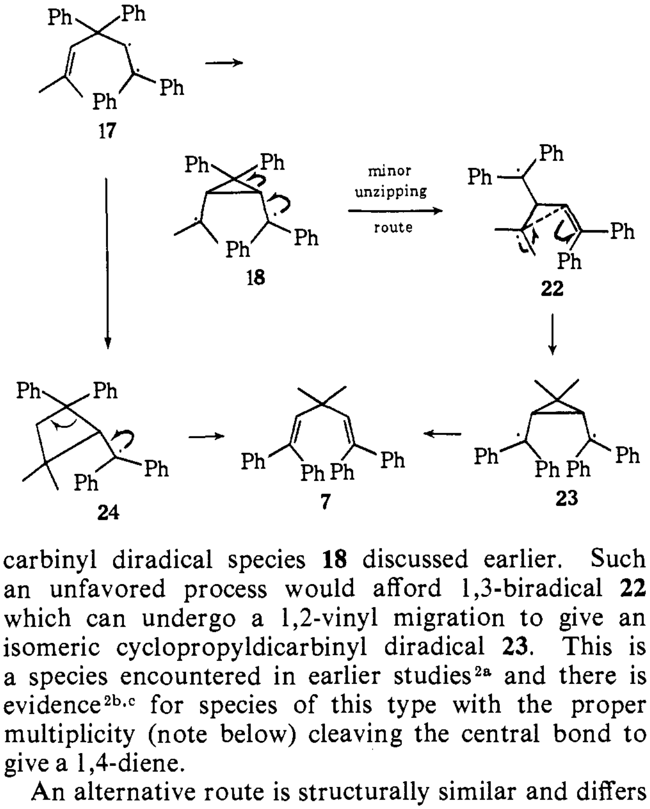
(19) (a) G. W. Griffin, A. F. Marcantonio, and H. Kristinsson, *Tetrahedron Lett.*, 2951 (1965); (b) H. Kristinsson and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 5969 (1967).

(20) (a) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 6096 (1968); (b) H. E. Zimmerman and C. O. Bender, *ibid.*, **92**, 4366 (1970). (c) An example of such a 1,3-vinyl migration does exist in the literature in a gas-phase mercury-sensitized photolysis; *cf.* J. Meinwald and G. W. Smith, *J. Amer. Chem. Soc.*, **89**, 4923 (1967). Here fission to give vinyl and allylic radicals, followed by recombination, was proposed.

ping process to give **19**, while the alternative process utilizing the benzhydryl odd electron results in loss of this source of energy lowering. It is interesting that such energetic effects are capable of controlling the course of reactions of excited state processes in spite of the rapidity of the transformations involved.

Another striking feature is the regiospecificity found in the phenyl migration route. Here phenyl migrates preferentially to the diphenylvinyl moiety rather than to the isopropylidene π system. This seems most reasonably ascribable to concentration of excitation energy and wave function perturbation in the diphenylvinyl portion of the excited state. Both singlet and triplet excitation energies are much lower for a styryl group than for an isolated double bond. Thus, one can argue that the isopropylidene bond orders, electron densities, and wave function are quite similar in the excited molecule to the corresponding properties of the unexcited molecule; thus there is no tendency of phenyl to migrate to this moiety. A third point is especially novel and fascinating. This regards the unusual[20c] formation of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**7**) in the sensitized runs. This seems most likely to derive from the less favored unzipping process (note Chart V) of the cyclopropyldicarbinyl diradical species **18** discussed earlier. Such an unfavored process would afford 1,3-biradical **22** which can undergo a 1,2-vinyl migration to give an isomeric cyclopropyldicarbinyl diradical **23**. This is a species encountered in earlier studies[2a] and there is evidence[2b,c] for species of this type with the proper multiplicity (note below) cleaving the central bond to give a 1,4-diene.

Chart V. Mechanism of Formation of 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene



An alternative route is structurally similar and differs primarily in the sequence in which bonds are formed and severed. This, too, is delineated in Chart V.

Reaction Efficiencies and Multiplicities. A number of conclusions are relatively straightforward when one considers the results of the direct and sensitized runs in conjunction (note Table I). First, from the observation of phenyl migration only in the direct irradiation and not in the sensitized runs, it is possible to conclude that phenyl migration occurs only from the singlet excited state. This conclusion is possible since the sensitized runs define the behavior of the triplet and these runs afford no phenyl migration.

Secondly, we know that the triplet gives especially efficient vinyl–vinyl bridging in contrast to most literature precedent for acylic dienes. It is generally the singlet excited state which undergoes vinyl–vinyl bridging and the triplet is usually unreactive.[2] However, the evidence reported by us earlier[2] strongly suggested that lack of triplet reactivity in acyclic di-π-methane systems was due to a "free rotor effect" in which electronic excitation energy was dissipated rapidly by rotation about an excited π bond of the triplet. In the present instance, one expects the unzipping process to be much more facile than usual due to the special stabilization afforded when electron density is deposited on the central phenyl-bearing carbon. Additionally, space-filling models show that the present system under study is quite cluttered and free rotation may be nearly as restricted as in the bicyclic literature examples where triplet energy is retained for reaction.

Still another conclusion is possible. This comes from observation of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**7**) only in sensitized runs. This product then is clearly formed only from the triplet and not from the singlet. Since this product is not found in the direct irradiations,. one is forced to conclude that intersystem crossing is quite inefficient and that the products which one does observe on direct irradiation must come heavily from the singlet. The phenyl migration product **6** already has been shown to arise from the singlet. But in the absence of the present evidence, the formation of the vinyl–vinyl bridging product **5** in the direct irradiation might have come, *a priori*, either from the singlet or from the triplet. That this product is known to be formed efficiently from independently generated triplet (*i.e.*, in sensitization) would have posed a dilemma. However, we now can conclude that the vinyl–vinyl bridging product **5** comes primarily from the singlet in direct irradiations and from the triplet in sensitized runs. The very high efficiency (Φ = 0.42) in the sensitized runs compared with a much lower efficiency (Φ = 0.076) in the direct runs suggests an advantage enjoyed by the triplet.

It has been noted by us earlier[2f] that the downward slope of a plot of energy *vs.* odd-electron separation is greater for a triplet than for a singlet where the molecular change is adiabatic (*i.e.*, no change in configuration), although the reverse is true for infinite separation to a double doublet where the higher energy S_1 has more to gain than T_1. The present photochemistry clearly involves odd electron separation conforming to the former situation. A final point is the failure of cyclooctadiene in altering the product ratio on direct irradiation. This suggests either that there are no triplets to be quenched or that the triplets rearrange exceedingly rapidly;[21] there is already evidence for the former.

Thus, one does note that control of excited state processes by appropriate substitution of delocalizing groups is possible. One can conclude that, despite the rapidity of many excited state rearrangements,[2d]

(21) Cyclooctadiene should have a cisoid-diene triplet energy approaching the 53 kcal/mol characteristic of cyclohexadiene, and this should be low enough to quench a diphenylvinyl triplet moiety (E_T = 62 kcal/mol for styryl).[15]

the excited state species can be diverted in one direction *vs.* another. The nature of this control is one of the most intriguing of phenomena.

Experimental Section[22]

Tetraphenylallene. This was prepared in 34% yield by the method of Vörlander and Siebert[23] from the pyrolysis of barium diphenylacetate and melted at 168–170° (lit.[23] mp 164–165°). The spectral data were: ir (KBr)[3] 6.30, 6.76, 6.96, 7.91, 8.69, 9.36, 9.75, 10.03, 10.36, 10.95, 11.19, 12.87, 13.13, 13.66, 14.50, 15.58 μ; uv $\lambda_{max}^{cyclohexane}$ 267 nm (ϵ 29,200). 246 (22,400).

2,2,4,4-Tetraphenyl-3-butenoic Acid. The following is a modification of the method of Schlenk and Bergmann[4] whose experimental description is a bit limited. Sodium shot (7.0 g, 304 mg-atoms, *ca.* 1 mm size prepared in toluene) was added to a solution of 5.0 g (14.6 mmol) of tetraphenylallene in ether (*ca.* 750 ml) freshly distilled from sodium–potassium alloy in a nitrogen atmosphere. The solution rapidly became deep red and, after stirring at room temperature for 1.5 hr, was pressure-transferred to a flask being swept with dry gaseous carbon dioxide. The color disappeared immediately on entering the flask and the transfer required 30 min. The ethereal solution was treated with 20 ml of methanol and then poured into 170 ml of 0.5 *N* sodium hydroxide. The resulting sodium salt was allowed to crystallize overnight and then filtered to yield 5.80 g of colorless crystals. This material was dissolved in 48 ml of 95% ethanol and treated with 13 ml of 2.4 *M* HCl in absolute ethanol.

After standing 10 hr, the solution was filtered and added to 300 ml of water; the separated acid, which crystallized after scratching the flask, was filtered and dried to give 4.81 g of crude material. A further 0.66 g could be obtained from the filtrate of the sodium salt by sodium hydroxide extraction and acidification. Recrystallization from heptane–ether gave 4.45 g (78%) of essentially pure 2,2,4,4-tetraphenyl-3-butenoic acid, mp 174.5–179.5°. Further recrystallization brought the melting point up to 181–182° (lit.[4] 179°). The spectral data were: nmr ($CDCl_3$) τ −1.4 (s, 1 H, acid), 2.45–3.43 (complex, 21 H, arom and vinyl); ir (KBr) 3.43, 3.82, 5.88 μ; uv λ_{max}^{EtOH} 253 nm (ϵ 16,600), 293 sh (722).

Anal. Calcd for $C_{28}H_{22}O_2$: C, 86.12; H, 5.68. Found: C, 86.14; H, 5.75.

Methyl 2,2,4,4-Tetraphenyl-3-butenoate. A solution of 2.08 g (5.3 mmol) of 2,2,4,4-tetraphenyl-3-butenoic acid in 100 ml of ether was slowly added to 250 ml of ethereal diazomethane (*ca.* 12 mmol) with ice cooling. After removal of excess diazomethane in a nitrogen stream and concentration, recrystallization from hexane yielded methyl 2,2,4,4-tetraphenyl-3-butenoate (1.91 g, 91.4%), mp 119.5° (lit.[4] mp 117–118°). The spectral data were: nmr ($CDCl_3$) τ 2.48–3.37 (complex, 21 H, arom and vinyl), 6.67 (s, 3 H, $-OCH_3$); ir (Fluorolube) 5.78 μ; uv λ_{max}^{EtOH} 253 nm (ϵ 17,100), 293 sh (739).

Anal. Calcd for $C_{29}H_{24}O_2$: C, 86.11; H, 5.98. Found: C, 86.27; H, 5.91.

2,2,4,4-Tetraphenyl-3-butenol. A solution of 5.36 g (13.3 mmol) of methyl 2,2,4,4-tetraphenyl-3-butenoate in 190 ml of anhydrous ether was added dropwise to a stirred solution of 0.54 g (13.5 mmol) of lithium aluminum hydride in 250 ml of anhydrous ether at room temperature. After the mixture was stirred for 2.5 hr, 11.0 g of a mixture of pulverized sodium sulfate decahydrate and Celite diatomaceous earth (*ca.* 1:1 by volume) was added and the suspension stirred overnight. The pure white suspension was filtered, the filtrate was concentrated *in vacuo*, and the residue was crystallized from hexane to yield 4.23 g (85%) of pure 2,2,4,4-tetraphenyl-3-butenol, mp 98–98.5°. The spectral data were: nmr (CCl_4) τ 2.7–3.5 (complex, 21 H, arom and vinyl), 6.21 (br, 2 H, CH_2), 8.98 (br, 1 H, OH); ir (CCl_4) 2.76, 2.86, 3.22, 3.25, 3.28, 3.35, 3.39, 3.45, 5.14, 5.32, 5.55, 6.26, 6.71, 6.92, 7.22, 7.49, 8.09, 8.45, 8.61, 9.44, 9.61, 10.71, 11.11, 14.37 μ; uv λ_{max}^{MeOH} 251 nm (ϵ 18,300).

Anal. Calcd for $C_{28}H_{24}O$: C, 89.32; H, 6.43. Found: C, 89.09; H, 6.24.

2,2,4,4-Tetraphenyl-3-butenal. Acetic anhydride (32.4 ml) was added with mixing to a solution of 6.00 g (15.93 mmol) of 2,2,4,4-tetraphenyl-3-butenol in 48 ml of distilled dimethyl sulfoxide. After standing for 22.5 hr, the solution was diluted with 107 ml of 95% ethanol and stirred for 1 hr, diluted with 26.8 ml of water, and cooled in ice as 70 ml of concentrated ammonium hydroxide was added. Then 107 ml of water was added and the resulting precipitate washed with water. After drying, crystallization from hexane gave 4.99 g (83.6%) of crystalline aldehyde, mp 138–143°. Recrystallization brought the melting point of the 2,2,4,4-tetraphenyl-3-butenal up to 141–142.5°. The spectral data were: nmr (CCl_4) τ 0.64 (s, 1 H, aldehyde), 2.7–3.4 (m, 21 H, arom and vinyl); ir (CCl_4) 2.89, 3.22, 3.25, 3.28, 3.52, 3.67, 5.13, 5.32, 5.54, 5.79, 6.26, 6.71, 6.92, 7.22, 7.32, 8.46, 8.64, 9.31, 9.68, 9.90, 10.92, 11.21, 11.31, 14.37, 14.96, 15.52 μ; uv λ_{max}^{EtOH} 252 nm (ϵ 14,400).

Anal. Calcd for $C_{28}H_{22}O$: C, 89.80; H, 5.92. Found: C, 89.75; H, 5.93.

1,1,3,3-Tetraphenyl-5-methyl-1,4-hexadiene. This procedure is a modification of that used by Wittig and Wittenberg[24] for the preparation of 1,1,1-triphenyl-4-methyl-3-pentene. To a well-stirred suspension of 4.865 g (11.25 mmol) of isopropyltriphenylphosphonium iodide[6] in 25 ml of anhydrous ether was added an ethereal solution of phenyllithium (*ca.* 11.25 mmol), and the now blood-red mixture was stirred for 2 hr. A solution of 4.00 g (10.68 mmol) of 2,2,4,4-tetraphenyl-3-butenal in a mixture of 40 ml of anhydrous ether and 40 ml of anhydrous benzene was added dropwise over 15 min, and stirring continued for 16 hr. Water was added, dissipating the red color, the solvents were removed *in vacuo*, and the residue was slurried in 32 ml of hot methylene chloride and chromatographed on a 3.0 × 80 cm column of activated silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh, heated at 125° for 16 hr) slurry-packed with 5% ether–hexane and washed with 1 l. of hexane. The desired diene was eluted with 12 l. of hexane and recrystallized from ethanol–methylene chloride to give 3.72 g (87%) of 1,1,3,3-tetraphenyl-5-methyl-1,4-hexadiene, mp 148–149.5°. The spectral data were: nmr (CCl_4) τ 2.5–3.4 (complex, 21 H, arom and $Ph_2C{=}CH-$), 4.38 (br, 1 H, $Me_2C{=}CH-$), 8.59 (d, J = 1.5 Hz, 3 H, CH_3), 8.78 (d, J = 1.5 Hz, 3 H, CH_3); ir (CCl_4) 3.22, 3.25, 3.28, 3.32, 3.39, 3.42, 3.48, 5.14, 5.33, 5.54, 6.04, 6.26, 6.71, 6.92, 7.22, 7.28, 8.45, 9.30, 9.69, 9.97, 10.61, 11.12, 14.36 μ; uv $\lambda_{max}^{cyclohexane}$ 255 nm (ϵ 18,250); mass spectrum (70 eV) *m/e* (rel intensity) 400 (20) parent, 357 (16), 233 (47), 167 (98), 91 (100); parent peak 400.232 (calcd for $C_{31}H_{28}$, 400.219).

Anal. Calcd for $C_{31}H_{28}$: C, 92.95; H, 7.05. Found: C, 93.08; H, 7.06.

Irradiation of 1,1,3,3-Tetraphenyl-5-methyl-1,4-hexadiene. A solution of 3.81 g (9.28 mmol) of 1,1,3,3-tetraphenyl-5-methyl-1,4-hexadiene in 2.5 l. of *tert*-butyl alcohol was purged with purified[25] nitrogen for 45 min before and then during the irradiation. The light source was a 450-W Hanovia medium-pressure lamp with a Corex glass filter (cutting off below 260 nm) all in a water-cooled immersion well. Irradiation was carried on for 1.75 hr, and after removing 100 ml of the resulting solution for separate analysis, the remainder was concentrated *in vacuo* to afford 3.68 g of yellow crystals. This crude material was chromatographed on a 4.5 × 80 Vycor column of silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) containing *ca.* 0.5% of lead and manganese doped calcium silicate phosphor (Sylvania No. 290). This was slurry-packed with 2% methylene chloride–hexane and eluted with 7 l. of 2% methylene chloride–hexane and 500 ml each of 5, 10, 20, 40, 60, and 80% methylene chloride–hexane.

The bands were monitored with a short wavelength uv hand lamp. The first band to elute (after 6750 ml) comprised 2.096 g of recovered starting material, and after a small overlap fraction (250 ml, 26 mg), the next 2250 ml eluted the second band which weighed 1.069 g and was a mixture of all the photoproducts. The mixture contained two major photoproducts (A and B) in the ratio of *ca.* 3:1, respectively, which were isolated and characterized as per below, and a minor product which was not isolated. This mixture did not separate on normal open column chromatography or on tlc. Columns tried included silica gel, alumina, silver nitrate on silica gel (tlc), tetranitrobenzylpolystyrene,[26] and reverse-phase liquid–liquid chromatography on polystyrene bead support.[2a] Successful separation of the photomixture is described below.

Separation of the Photomixture. Analytical. In spite of the high molecular weight (400), the photoisomers were successfully separated by glpc. A glass column 2 m × 2 mm i.d. packed with 2% SE-54 (Varian) on Chromosorb W, non-acid-washed, 60–80 mesh (column A), separated the major products B and A from each other and from the starting material. Typical retention times were 10.3, 11.3, and 17.7 min, respectively, at 185° and carrier flow of *ca.*

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[22] All melting points were taken on a hotstage apparatus calibrated with known compounds.

[23] D. Vorländer and C. Siebert, *Chem. Ber.*, **39**, 1024 (1906).

[24] G. Wittig and D. Wittenberg, *Justus Liebigs Ann. Chem.*, **606**, 1 (1957).

[25] L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

[26] J. T. Ayres and C. K. Mann, *ibid.*, **38**, 859, 861 (1966).

50 ml per min. Also used successfully was high-pressure liquid–liquid chromatography. An ALC-100 liquid chromatograph (Waters Associates) equipped with three 2 ft × $^{1}/_{8}$ in. columns packed with Corasil/C18 (a nonpolar stationary phase permanently bonded to high surface area glass beads) (column B) and eluted with 58% acetonitrile–water[27] (v/v) at 0.6 ml/min gave retention times of 34, 42, and 72 min for the photoproducts A and B and starting material, respectively. The liquid chromatograph was calibrated with the pure photochemical reactant and products, and an internal standard (1,4-diphenyl-1,3-butadiene) was used for analysis of the quantum yield runs.

Separation of the Photomixture. Preparative. Liquid chromatography was again used for preparative separation of the photoisomers. A system was used which was composed of a simple positive displacement, low-volume pump, a pulse damper, an in-line injection port, the desired column, a variable wavelength ultraviolet scanner with special low-volume high sensitivity flow-through cell, topped off with a fraction collector. The column packing was a nonpolar stationary phase permanently bonded to sponge surfaced glass beads prepared as detailed below. In a typical separation, 1.72 g of photoisomers was dissolved in 17 ml of acetonitrile (acetone also works well) and injected in *ca.* 50-mg aliquots. The system was two 6 ft × $^{3}/_{8}$ in. columns of nonpolar stationary phase on sponge surfaced glass beads in series (column C) using 60% acetonitrile–water (v:v) at 2 ml/min as the mobile phase. The column was overloaded under these conditions, but the overlapping peaks were cut at the minimum to give *ca.* 90% separation in minimum time. The collected eluate was concentrated *in vacuo*, diluted with water, and extracted several times with ether to recover the products. The first peak yielded 1.137 g of product A contaminated with *ca.* 10% of product B.

Numerous recrystallizations from ethanol–methylene chloride yielded pure 1,1,2,2-tetraphenyl-3-(2-methylpropenyl)cyclopropane, mp 143.5–144.5°. The spectral data were: nmr (CCl_4) τ 2.6–3.4 (complex, 20 H, arom), 4.96 (br d, J = 9.5 Hz, 1 H, vinyl), 6.49 (d, J = 9.5 Hz, 1 H, cyclopropyl), 7.96 (d, J = 1 Hz, 3 H, CH_3), 8.21 (d, J = 1 Hz, 3 H, CH_3); ir (KBr) 3.38, 3.32, 3.39, 3.45, 6.26, 6.69, 6.95, 7.27, 8.68, 9.32, 9.75, 11.69, 12.70, 13.40, 13.72, 14.32 μ; uv $\lambda_{\mathrm{sh}}^{\mathrm{cyclohexane}}$ 225nm (ϵ 27,400), 269 (1820), 275 (1005); mass spectrum (70 eV) *m/e* (rel intensity) 400 (30) parent, 357 (23), 233 (63), 167 (100), 165 (63), and 91 (74); parent peak 400.232 (calcd for $C_{31}H_{28}$, 400.219).

Anal. Calcd for $C_{31}H_{28}$: C, 92.95; H, 7.05. Found: C, 92.90; H, 7.07.

The second peak yielded 339 mg of product B contaminated with *ca.* 10% of product A. In this case, recrystallization failed to remove the residual contaminant, so this material was rechromatographed in the manner described above and then recrystallized from ethanol–methylene chloride to give pure 1,1,2,3-tetraphenyl-2-(2-methylpropenyl)cyclopropane (B), mp 136–137°. The spectral data were: nmr ($CDCl_3$) τ 2.6–3.2 (complex, 20 H, arom), 3.88 (br s, 1 H, vinyl), 6.06 (s, 1 H, cyclopropyl), 8.47 (d, J = 1, 3 H, CH_3), 9.24 (d, J = 1, 3 H, CH_3); ir (KBr) 3.28, 3.32, 3.45, 6.26, 6.69, 6.95, 7.29, 8.68, 9.32, 9.76, 11.16, 12.46, 12.97, 13.14, 13.50, 14.36 μ; uv $\lambda_{\max}^{\mathrm{cyclohexane}}$ 228 nm (ϵ 29,300), 267 sh (1630), 274 sh (914); mass spectrum (70 eV) *m/e* (rel intensity) 400 (32) parent, 357 (56), 255 (48), 233 (35), 167 (91), 165 (49), 145 (76), 129 (47), 128 (40), and 91 (100); parent peak 400.218 (calcd for $C_{21}H_{28}$, 400.219).

Anal. Calcd for $C_{31}H_{28}$: C, 92.95; H, 7.05. Found: C, 92.80; H, 7.17.

Sponge Surfacing of Glass Beads. One kilogram of glass microbeads (Cataphote Corp., soda-lime glass, 44–62 μ) was added to a warm solution of 360 g of sodium hydroxide in 1500 ml of water (*ca.* 6 *N*) and the mixture rapidly brought to reflux with stirring. After 1 hr, the mixture was poured into cold water to quench the reaction and the beads were washed with water by decantation until the supernatant liquid remained clear. After washing several times with acetone, the beads were air-dried in a hot air oven at 65°. Under the optical microscope these beads appear to have a frosty crust. The surface is believed to be a sponge-like layer, 2–4 μ thick, with sodium silicate bonds available. Shorter reflux times gave coatings that appear thinner, with the thickness controllable by reaction time. The beads were either coated with stationary phase or treated with silicon tetrachloride which rendered the silica sponge especially stable and mechanically strong.

Bonding a Nonpolar Material to the Sponge Surfaced Beads. Sponge surfaced beads (140 g) were slurried with octadecyltrichlorosilane (13.72 g, 9.8% of the bead weight) in hexane. The solvent was slowly removed on a rotary evaporator to leave dry, free-flowing beads. These were rolled with heating (90°) while purging the vessel with dry nitrogen for 5 hr. Exhaustive extraction of a sample of these beads with chloroform indicated that the beads retained *ca.* 4% stationary phase. After rinsing the bulk of the beads several times with chloroform, they were treated with chlorotrimethylsilane in hexane and dried. After being packed into 6 ft × $^{3}/_{8}$ in. stainless steel columns, it was found necessary to flush the columns with chloroform at 3 ml/min for 16 hr before use in order to achieve maximum efficiency. These columns have been used for several months with aqueous acetonitrile solvent, plus occasional flushing with chloroform, with no sign of deterioration.

Characterization of 1,1,2,2-Tetraphenyl-3-(2-methylpropenyl)-cyclopropane. Degradation to 2,2,3,3-Tetraphenylcyclopropanecarboxylic Acid and Acetone. The method used was based on that described by von Rudloff.[10] A solution containing 1.05 g of sodium metaperiodate, 30 mg of potassium permanganate, and 50 mg of potassium carbonate in 50 ml of water was added to a solution of 100 mg of 1,1,2,2-tetraphenyl-3-(2-methylpropenyl)cyclopropane in 50 ml of dioxane. The mixture was stirred at room temperature for 3 hr, after which time *ca.* 5 ml of solvent was distilled under reduced pressure into a Dry Ice cooled trap. This material was treated with 1 ml of 2,4-dinitrophenylhydrazine reagent and diluted with water, whereupon orange crystals precipitated out. These were filtered, washed with water, dried, and recrystallized from 95% ethanol to mp 125.5°. This material gave nmr and ir spectra which were identical in all respects with those of authentic acetone 2,4-dinitrophenylhydrazone (mp 126°).[28] The remainder of the reaction mixture was treated with 1 g of sodium hydroxide and extracted three times with 50 ml of ether; the combined extracts were washed three times with 50 ml of water, dried, and concentrated to 44 mg of crude material which was crystallized from hexane–methylene chloride to give 22 mg (26%) of a neutral compound (mp 205–207°) characterized as 1,1,2,2-tetraphenylcyclopropanecarboxaldehyde. The spectral data were: nmr ($CDCl_3$) τ 0.80 (d, J = 7 Hz, 1 H, aldehyde), 2.28–2.64 (complex, 4 H, arom), 2.64–3.12 (complex, 16 H, arom), 6.42 (d, J = 7 Hz, cyclopropyl); ir (KBr) 3.5, 5.96 μ.

The aqueous phase was acidified to Congo Red with hydrochloric acid and extracted five times with 50 ml of ether; the combined extracts were washed three times with 50 ml of water, dried, and concentrated to 88 mg of an oil. Crystallization from hexane–methylene chloride and sublimation at 200° (1 mm) gave 61 mg (63%) of 2,2,3,3-tetraphenylcyclopropanecarboxylic acid, mp 251–253° (sealed capillary). The spectral data were: nmr ($CDCl_3$) τ 1.66 (br, 1 H, acid), 2.51–3.25 (complex, 20 H, arom), 6.30 (s, 1 H, cyclopropyl); ir (KBr) 3.1–4.4 (br), 5.87 (cyclopropyl acid), 6.26, 6.72, 6.99, 8.10, 8.27, 8.66, 9.30, 9.74, 11.08, 11.27, 12.68, 13.86, 14.36 μ; uv $\lambda_{\max}^{\mathrm{EtOH}}$ 223 nm (ϵ 21,500); mass spectrum (70 eV) *m/e* (rel intensity) 390 (3) parent, 344 (23), 331 (33), 330 (100), 267 (33), 223 (8), 167 (17.5), 165 (25).

Anal. Calcd for $C_{28}H_{22}O_2$: C, 86.12; H, 5.68. Found: C, 85.98; H, 5.63.

Methyl 2,2,3,3-Tetraphenylcyclopropanecarboxylate. A solution of 475 mg (1.22 mmol) of 2,2,3,3-tetraphenylcyclopropanecarboxylic acid in 50 ml of ether and 25 ml of dichloromethane was treated with 100 ml of ethereal diazomethane (*ca.* 4 mmol). After removal of excess diazomethane in a nitrogen stream and concentration, the crude ester was chromatographed on a 1 × 45 cm column of silica gel with 3% ether–hexane. The single band obtained was concentrated, and recrystallized from hexane to give 384 mg (78%) of methyl 2,2,3,3-tetraphenylcyclopropanecarboxylate, mp 131–132°. The spectral data were: nmr ($CDCl_3$) τ 2.53–3.25 (complex, 20 H, arom), 6.27 (s, 1 H, cyclopropyl), 6.44 (s, 3 H, $-OCH_3$); ir (KBr) 3.27, 3.31, 3.34, 3.40, 5.78, 6.28, 6.72, 6.94, 7.00, 7.24, 8.16, 8.38, 8.54, 8.99, 9.30, 9.67, 9.90, 12.86, 13.47, 14.23 μ; mass spectrum (70 eV) *m/e* (rel intensity) 404 (2) parent, 344 (41), 330 (100), 267 (42), 265 (17), 167 (17), 165 (35), 91 (6).

Degradation of Methyl 2,2,3,3-Tetraphenylcyclopropanecarboxylate. Cyclopropane Cleavage. A solution of 500 mg (1.24 mmol) of methyl 2,2,3,3-tetraphenylcyclopropanecarboxylate in 10 ml of anhydrous tetrahydrofuran was added to a refluxing solution of 18.9 mg (2.70 mg-atoms) of lithium in *ca.* 10 ml of anhydrous liquid ammonia. The deep blue solution turned to deep red and finally to deep green. After the mixture was stirred for 30 min, solid am-

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[27] We thank Mr. James Waters for suggesting this solvent and reporting successful separation under these conditions.

[28] "Sadtler Standard Spectra," Sadtler Research Laboratories, Philadelphia, Pa.

monium chloride was added until the solution decolorized (*ca.* 300 mg), and the ammonia was allowed to evaporate. After solvent removal *in vacuo*, the reaction mixture was taken up in 100 ml of ether and 100 ml of water and the layers were separated. The aqueous layer was extracted twice with 50 ml of ether, and the combined extracts were washed twice with 50 ml of water, dried, and concentrated to 485 mg of slightly brown oil.

This crude product mixture was subjected to column chromatography on a 2.5 × 35 cm column of silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) slurry-packed with 3% ether in hexane and eluted with the same solvent into 125-ml fractions. Fraction 1 contained 49 mg of a 90:10 mixture of diphenylmethane (identified by comparison with an authentic sample by ir and nmr spectra, retention volume on high-pressure liquid chromatography (column B), and retention time on glpc (columns A and D)) and methyl 3,3-diphenyl-2-(diphenylmethyl)-2-propenoate, respectively.

Fractions 2–5 contained 381 mg of a mixture of esters. Crystallization from hexane gave 172 mg of a single ester, methyl 3,3-diphenyl-2-(diphenylmethyl)-2-propenoate, characterized by its spectral data and reduction to the methyl ester of the known dibenzhydrylacetic acid[11] (*vide infra*). Recrystallization from hexane gave 133 mg of pure material, mp 132.5–133.5°. The spectral data were: nmr (CCl_4) τ 2.8 (pseudo-doublet, 20 H, arom), 4.81 (s, 1 H, Ph_2CH–), 6.94 (s, 3 H, OCH_3); ir (CCl_4) 3.25, 3.28, 3.32, 5.83, 6.28, 6.72, 6.94, 7.00, 7.60, 7.68, 8.00, 8.14, 9.00. 9.33, 9.73, 10.28, 10.98, 14.34 μ; mass spectrum (70 eV) *m/e* (rel intensity) 405 (12), 404 (38) parent, 344 (71), 330 (51), 267 (48), 167 (82), 165 (61), 69 (55), 57 (100), 56 (80).

Anal. Calcd for $C_{29}H_{24}O_2$: C, 86.11; H, 5.98. Found: C, 86.07; H, 5.98.

The remainder of the mixture of esters was subjected to preparative high-pressure liquid chromatography (column C) and separated into three substantial peaks. The first peak yielded 46 mg of methyl 3,3-diphenylpropionate, identified by comparison of its nmr and ir spectra with those of authentic material (*vide infra*). The second peak yielded 85 mg of a binary mixture of which 40% was determined to be methyl dibenzhydrylacetate by nmr analysis. The nmr spectrum of the remaining component is consistent with 1,1,4,4-tetraphenyl-2-butanone (ir on mixture showed strongest C=O at 5.82 μ (saturated ketone), weaker one at 5.78 μ (saturated ester), but no attempt was made to isolate and further characterize this compound.

The third peak consisted of 76 mg of a ternary mixture, the major component being residual methyl 3,3-diphenyl-2-(diphenylmethyl)-2 propenoate, and the remaining two components being overlap from the second peak. The total yields, based on isolation and nmr analysis of mixtures, were: methyl 3,3-diphenyl-2-(diphenylmethyl)-2-propenoate (42%), diphenylmethane (20%), methyl 3,3-diphenylpropionate (15%), 1,1,4,4-tetraphenyl-2-butanone (15%), and methyl dibenzhydrylacetate (10%).

Methyl Dibenzhydrylacetate. Reduction of Methyl 3,3-Diphenyl-2-(diphenylmethyl)-2-propenoate. A solution of 120 mg (0.297 mmol) of methyl 3,3-diphenyl-2-(diphenylmethyl)-2-propenoate in 7 ml of anhydrous tetrahydrofuran was added to 15 ml of refluxing anhydrous ammonia, followed by 4.6 mg (0.653 mg-atom) of lithium. The mixture was stirred for 75 min during which time the solution turned intense red, then deep green. Solid ammonium chloride was added to decolorize the solution (*ca.* 300 mg) and the ammonia was allowed to evaporate. After solvent removal *in vacuo*, the reaction mixture was taken up in 100 ml of ether and 100 ml of water, and the layers were separated. The aqueous layer was extracted twice with 50 ml of ether, and the combined extracts were washed with 50 ml of water, dried, and concentrated to give 120 mg of brown oil. This was chromatographed on a 1 × 45 cm column of silica gel with 3% ether–hexane to give an early band containing 6 mg of diphenylmethane and a main band of 109 mg. Recrystallization from hexane gave 59 mg (49%) of pure methyl dibenzhydrylacetate, mp 100–100.5°. The spectral data were: nmr (CCl_4) τ 2.66–3.12 (complex, 20 H, arom), 5.82 (m, 3 H, benzhydryls and methine), 7.01 (s, 3 H, OMe); nmr using 0.6 molar ratio of $Eu(fod)_3$ shift reagent (C_6D_6) 1.85 (br d, J = 7 Hz, 4 H, one set of diastereotopic ortho hydrogens), 2.24 (br d, J = 7 Hz, remaining ortho hydrogens), 2.72–3.12 (complex, 12 H, remaining arom), 3.74 (t, J = 9 Hz, 1 H, methine), 4.3 (d, J = 9 Hz, 2 H, benzhydryl), 5.83 (s, 3 H, OMe); ir (KBr) 3.28, 3.10, 3.34, 3.40, 3.47, 5.78, 6.32, 6.73 6.92, 7.00, 7.60, 7.95, 8.26, 8.18, 9.23, 9.74, 10.99, 11.94, 12.46, 13.31, 13.50, 14.28, 14.41 μ; mass spectrum (70 eV) *m/e* (rel intensity) 406 (very weak) parent, 239 (very strong), 167 (base, offscale).

Anal. Calcd for $C_{29}H_{26}O_2$: C, 85.68; H, 6.45. Found: C, 85.64; H, 6.32.

Dibenzhydrylacetic Acid. Hydrolysis of Methyl Dibenzhydrylacetate. Methyl dibenzhydrylacetate (40 mg, 0.01 mmol) was treated with 200 mg of potassium hydroxide in 6 ml of boiling diethylene glycol for 16 hr. Upon cooling, the reaction mixture was diluted with water and extracted with ether to afford, after concentration *in vacuo*, a viscous brown oil. Crystallization from 95% ethanol gave 12 mg of dibenzhydrylacetic acid, mp 177–178° (lit.[11] 182.5–183.5°). This material was identical in all respects with authentic dibenzhydrylacetic acid (*vide infra*). The spectral data were: nmr (CCl_4) τ 4.23 (s, 3 H, benzhydryl H and methine H), 7.10 (complex, 20 H, arom), 8.0 (br s, 1 H, $-CO_2H$); ir ($CDCl_3$) 3.22, 3.25, 3.28, 3.37, 3.40, 3.48, 5.86, 6.34, 6.50, 6.70, 6.90, 7.78, 7.98, 9.00 (broad), 9.33 (broad), 9.94 (broad), 12.20–13.60 (broad), 13.80, 14.30 μ.

Dibenzhydrylacetic Acid. Dibenzhydrylacetic acid was prepared from ethyl acetoacetate and diphenylmethyl bromide according to Cope[11] and melted at 177–178°.

Methyl 3,3-Diphenylpropionate. Cinnamic acid was treated with benzene and anhydrous aluminum chloride according to Dippy[29] to give 3,3-diphenylpropionic acid. Treatment of this material with diazomethane gave methyl 3,3-diphenylpropionate. The spectral data were: nmr (CCl_4) τ 2.84 (m, 10 H, arom), 5.50 (t, J = 8 Hz, 1 H, benzhydryl), 6.52 (s, 3 H, OMe), 7.06 (d, J = 8 Hz, 2 H, CH_2CO_2Me); ir (neat film) 3.22, 3.25, 3.28, 3.31, 3.37, 3.41, 3.50, 5.14, 5.35, 5.76, 6.26, 6.70, 6.91, 6.98, 7.33, 7.59, 7.96, 8.38, 8.65, 9.02, 9.22, 9.72, 9.36, 9.49, 10.12, 10.44, 11.14, 11.99, 12.64, 13.24, 13.44, 14.34, 16.0 μ.

Characterization of 1,1,2,3-Tetraphenyl-2-(2-methylpropenyl)-cyclopropane. 1,2,2,3-Tetraphenylcyclopropanecarboxaldehyde. A mixture of 473 mg (1.18 mmol) of 1,1,2,3-tetraphenyl-2-(2-methylpropenyl)cyclopropane and 335 mg (1.32 mmol) of osmium tetraoxide in 125 ml of anhydrous ether was stirred at room temperature for 96 hr. After removal of the solvent in a nitrogen stream, the black osmate ester was hydrolyzed by refluxing in a solution of 3.00 g of sodium bisulfite in 100 ml of 95% ethanol for 5 hr with stirring. After cooling to room temperature, the inorganic material was removed by filtration and the organic filtrate diluted with ether, washed with water, dried, and concentrated to 522 mg of clear oil which was shown by ir and nmr to contain the desired glycol. Purification of this material was not attempted.

A mixture of the crude glycol (522 mg), 1.83 g of 82% lead tetraacetate (assayed titrimetrically), and 1.00 g of sodium acetate was stirred at room temperature in 50 ml of anhydrous acetone for 48 hr. The reaction mixture was filtered, and the filtrate was diluted with ether, washed with water, dried, and concentrated to afford 480 mg of a clear oil. This material was chromatographed on a 2.5 × 90 cm column of silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) slurry-packed with 1% ether–hexane; 250-ml fractions were collected. Fractions 3 and 4 yielded 183 mg of a solid, and fractions 8–10 gave 238 mg of a solid.

Fractions 3 and 4 after recrystallization from hexane yielded 142 mg of unreacted vinylcyclopropane, mp 136–137°.

Fractions 8–10 after recrystallization from hexane afforded 198 mg of a solid, mp 155–157°, characterized as 1,2,2,3-tetraphenylcyclopropanecarboxaldehyde. The spectral data were: nmr ($CDCl_3$) τ 0.57 (s, 1 H, aldehyde), 2.40–3.20 (complex, 20 H, arom), 5.64 (s, 1 H, cyclopropyl); ir (KBr) 3.25, 3.28, 3.31, 3.43, 3.52, 3.65, 5.93 (cyclopropyl aldehyde), 6.28, 6.73, 6.95, 7.25, 7.27, 7.60, 7.80, 8.70, 9.33, 9.75, 10.05, 10.35, 12.57, 13.00, 13.31, 13.65, 14.33, 15.84 μ; mass spectrum (70 eV) *m/e* (rel intensity) 374 (49) parent, calcd for $C_{28}H_{22}O$ 374.167, found 374.169; 283 (19), 267 (22), 265 (16), 252 (14), 207 (20), 191 (29), 179 (49), 178 (36), 167 (24), 165 (100), 152 (18), 94 (32), 91 (10); uv λ_{sh}^{MeOH} 258 nm (ϵ 2,420), 292 (ϵ 173).

3,4,5,5-Tetraphenyldihydrofuran. Thermal Rearrangement of 1,2,2,3-Tetraphenylcyclopropanecarboxaldehyde. A solution of 52.0 mg of 1,2,2,3-tetraphenylcyclopropanecarboxaldehyde in 5 ml of xylene was refluxed for 2 hr. Removal of the xylene by vacuum pumping gave a quantitative yield of 3,4,5,5-tetraphenyldihydrofuran. One recrystallization from hexane gave the pure compound, mp 131–132°. Spectral properties were: nmr (CCl_4) τ 2.2–3.3 (m, 21 H, arom and vinyl), 5.02 (s, 1 H, benzylic); ir (CS_2) 3.23, 3.26, 3.29, 6.13, 7.70, 8.47, 8.78, 9.42, 9.70, 9.80, 10.30, 11.40, 13.28, 14.40 μ.

Anal. Calcd for $C_{28}H_{22}O$: C, 89.80; H, 5.92. Found: C, 89.75; H, 5.83.

3-Keto-1,1,2,3-tetraphenylpropyl Formate. Oxidative Cleavage of 3,4,5,5-Tetraphenyldihydrofuran. To a solution of 59.3 mg

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[29] J. F. Dippy and J. T. Young, *J. Chem. Soc.*, 1817 (1952).

(0.234 mmol) of osmium tetroxide in 2 ml of ether and 1 ml of pyridine was added 52 mg (0.139 mmol) of 3,4,5,5-tetraphenyldihydrofuran in 1 ml of ether. The reaction was left stirring for 2 hr and then filtered to obtain the precipitated osmate ester. This precipitate was refluxed for 5 hr with 90 mg of sodium bisulfite in 7 ml of 95% ethanol. The reaction was again filtered and the filtrate washed with 50 ml of ether. The ether was washed with 2 × 25 ml of water and dried over magnesium sulfate, and the solvent was removed to give 52.3 mg of a white solid, mp 202–204°, whose spectral properties were consistent with those of the expected diol.

The crude diol was then treated with 133 mg of lead tetraacetate, 100 mg of sodium acetate, and 5 ml of acetone for 20 hr. The reaction was then filtered and the filtrate washed with 50 ml of ether. The ether was extracted with 2 × 25 ml of water and 2 × 25 ml of 5% sodium bicarbonate solution and dried over magnesium sulfate; the solvent was removed to give 48 mg (0.118 mmol, 85%) of 3-keto-1,1,2,3-tetraphenylpropyl formate. One crystallization from hexane gave the pure compound, mp 151–153°. Spectral properties were: nmr ($CDCl_3$) τ 1.61 (s, 1 H, formate), 2.0–3.2 (m, 20 H, arom), 4.25 (s, 1 H, benzylic); ir ($CHCl_3$) 3.23, 3.25, 3.29, 5.77, 5.92, 6.26, 6.32, 6.70, 6.92, 7.45, 8.21, 8.88, 9.28, 9.50, 9.68, 10.23, 14.35 μ; mass spectrum (70 eV) *m/e* (rel intensity) 360 (11.3) (calcd for $C_{27}H_{20}O$, 360.152; found 360.151), 359 (5.6), 256 (9.7), 255 (8.9), 182 (25.8), 167 (16.1), 105 (100), 77 (37.1), 46 (8.0).

Hydrolysis of 3-Keto-1,1,2,3-tetraphenyl Formate. A solution of 48 mg of 3-keto-1,1,2,3-tetraphenyl formate in 10 ml of 0.05 *N* potassium hydroxide in ethanol was refluxed for 5 min. The reaction was then poured into 75 ml of water and extracted with 2 × 25 ml of ether. The ether was washed with 25 ml of water and 25 ml of 1 *N* HCl and dried over magnesium sulfate, and the solvent was removed to give 39 mg of a yellow oil. This material was chromatographed on a 2.8 × 85 mm column of Matheson Coleman and Bell, Grade 62, 60–200 mesh, silica gel using 5% ether in hexane to elute. The eluent was collected in 25 ml fractions and monitored by scanning at 260 nm. Fractions 34–39 contained 10.8 mg of benzophenone; fractions 40–44, 8.9 mg of overlap; fractions 45–51, 16.4 mg of desoxybenzoin. These were identified by spectral comparison with authentic samples.

Photolysis Apparatus for Quantum Yields. The Black Box irradiation apparatus[14] used a GE AH6 high-pressure mercury arc centered at the focus of a parabolic aluminum reflector. The light was focused through a cell containing three water-cooled compartments for filter solutions. The photolysis cell consisted of two identical coaxial compartments, each 12 cm in diameter with a 5-cm optical path and aliphatic epoxy (uv transparent and nonfluorescent) cemented quartz faces. The cells were equipped with a thermistor probe inlet, Trubore stirrer, heat exchanger coil, and nitrogen inlet. A third cell was situated perpendicular to the main optical path to receive the light from a beam splitter consisting of a quartz plate mounted at 45° to the light path. This side cell was used to monitor light input to the photolysis cell. For 1 hr before and during irradiation, vanadous-purified nitrogen[26] was bubbled through the photolysis solution.

Actinometry. Each determination required three runs: (1) actinometer solution in the main sample cell and in the side cell, (2) reactant solution in the main cell and actinometer solution in the back cell and side cell, and (3) actinometer solution in the main cell and the side cell. In runs 1 and 3, the ratio of transmitted light to reflected light was determined, and this ratio along with the amount of light reflected during run 2 was used to calculate the lamp output during run 2. The amount of light transmitted to the back cell was substracted from this value to obtain the net light absorption. Potassium ferrioxalate actinometry[30] was employed.

Filter Solutions. Two filter solutions were used. Filter I had cell 1 containing 1.0 *M* nickel sulfate hexahydrate in 5% aqueous sulfuric acid; cell 2 containing 1.0 *M* cobalt sulfate heptahydrate in 5% aqueous sulfuric acid; and cell 3 containing 0.0002 *M* (0.063 g/l.) bismuth trichloride in 10% aqueous hydrochloric acid. The uv transmission of this filter was from 245 to 312 nm, with a maximum at 282 nm. In filter II, cells 1 and 2 contained the same solutions as filter I; cell 3 contained 0.015 *M* stannous chloride dihydrate in 5% aqueous hydrochloric acid. The uv transmission of this filter was from 295 to 360 nm, with a maximum at 322 nm.

Quantum Yield Procedures. Dilute solutions of 0.002 *M* of 1,1,3,3-tetraphenyl-5-methyl-1,4-hexadiene were irradiated in *tert*-butyl alcohol (freshly distilled from calcium hydride). Filter I was used in runs 1–3 and in runs Q1 and Q2. Filter II was used in runs 4 and 5. Sensitizer and quencher were added as noted. The Black Box apparatus was employed. High-pressure liquid chromatography analysis on column B was used after concentration *in vacuo* and addition of an internal standard. Additionally, product in the various runs was characterized both by the high-speed liquid chromatography and by vpc (columns A and D of 2% QF-1 on Varaport 30). Sensitized runs 4 and 5 were 0.31 *M* in acetophenone. Data for individual quantum yields are listed as follows: mass of starting material, light absorbed, total conversion, calculated mass of product, and quantum yield of product.

Run 1: 1,1,3,3-Tetraphenyl-5-methyl-1,4-hexadiene, 601 mg (1.50 mmol), 4.76 mEinsteins, 43% conversion; 133 mg (0.332 mmol) of 1,1,2,2-tetraphenyl-3-(2-methylpropenyl)cyclopropane, $\Phi = 0.070$; 85 mg (0.212 mmol) of 1,1,2,3-tetraphenyl-2-(2-methylpropenyl)cyclopropane, $\Phi = 0.045$.

Run 2: 1,1,3,3-Tetraphenyl-5-methyl-1,4-hexadiene, 600 mg (1.50 mmol), 1.94 mEinsteins, 28% conversion; 57 mg (0.143 mmol) of 1,1,2,2-tetraphenyl-3-(2-methylpropenyl)cyclopropane, $\Phi = 0.074$; 34 mg (0.0875 mmol) of 1,1,2,3-tetraphenyl-2-(2-methylpropenyl)cyclopropane, $\Phi = 0.044$.

Run 3: 1,1,3,3-Tetraphenyl-5-methyl-1,4-hexadiene, 600 mg (1.50 mmol), 0.687 mEinstein, 6% conversion; 21 mg (0.0525 mmol) of 1,1,2,2-tetraphenyl-3-(2-methylpropenyl)cyclopropane, $\Phi = 0.076$; 14 mg (0.035 mmol) of 1,1,2,3-tetraphenyl-2-(2-methylpropenyl)cyclopropane, $\Phi = 0.051$.

Run 4: Sensitized. 1,1,3,3-Tetraphenyl-5-methyl-1,4-hexadiene, 600 mg (1.50 mmol), 3.16 mEinsteins, 55% conversion; 323 mg (0.808 mmol) of 1,1,2,2-tetraphenyl-3-(2-methylpropenyl)cyclopropane, $\Phi = 0.25$; 8 mg (0.020 mmol) of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene, $\Phi = 0.006$.

Run 5: Sensitized. 1,1,3,3-Tetraphenyl-5-methyl-1,4-hexadiene, 600 mg (1.50 mmol), 0.643 mEinstein, 19% conversion; 109 mg (0.272 mmol) of 1,1,2,2-tetraphenyl-3-(2-methylpropenyl)-cyclopropane, $\Phi = 0.42$; 2.6 mg (0.0065 mmol) of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene, $\Phi = 0.01$.

Quenched runs were used to give the relative areas of 1,1,2,2-tetraphenyl-3-(2-methylpropenyl)cyclopropane (**5**) and 1,1,2,3-tetraphenyl-2-(2-methylpropenyl)cyclopropane (**6**), and these areas were compared with unquenched run areas: (run 1) no quencher, 43% conversion, 1.8 relative area $^5/_6$; (run 2) no quencher, 28%, 2.0; (run Q1) 0.5 *M* 1,3-cyclooctadiene, 17%, 1.9; (run Q2) 1.87 M, 28%, 1.7, uncertainty ±0.1.

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