The Di-π-methane Rearrangement. Interaction of Electronically Excited Vinyl Chromophores. Mechanistic and Exploratory Organic Photochemistry. XLI[1]

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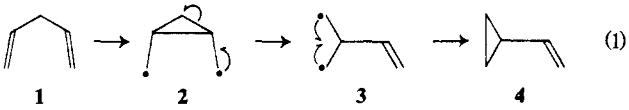
Abstract: The divinyl version of the di-π-methane rearrangement described by us earlier was extended to an acyclic system in order to elucidate the nature of the rearrangement as a function of structure. Thus, 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**5**) was synthesized; on direct irradiation **5** afforded 1,1-diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane (**8**) as the sole primary photoproduct. Isotope dilution analysis was employed for quantum yield studies and a method of efficiently introducing tritium into the diene **5** was developed. The unsensitized quantum yield, 0.080, indicated a reaction of modest efficiency. Triplet energy transfer from benzophenone was shown to occur efficiently by inhibition of the benzophenone–benzhydrol photoreaction on addition of the divinylmethane **5**. Strikingly, despite triplet energy transfer and excitation of **5**, benzophenone sensitization of the divinylmethane rearrangement proved to be much less efficient than direct irradiation. Propiophenone sensitization was found to be only slightly more efficient. Chlorobenzene, of still higher triplet energy, effected a sensitized reaction with the same efficiently as propiophenone. It is concluded that triplet states of **5** of energy below *ca.* 80 kcal/mol, including T_1, give rise to a much less efficient rearrangement than the excited state responsible in the direct irradiation. The excited state giving rise to the divinylmethane rearrangement upon direct irradiation is most reasonably formulated as the singlet, S_1. The present acyclic di-π-methane is contrasted with the geometrically constrained bicyclic di-π-methane systems in both singlet and triplet reactivity, and the mechanism is discussed in molecular and electronic detail.

In a recent series of publications[2,3] we noted that molecules having the di-π-methane moiety, *i.e.*, having two π systems bonded to a single sp^3 carbon, undergo a general[4] liquid phase photochemical transformation to vinylcyclopropanes. We suggested that the gross mechanism followed involves vinyl–vinyl bridging (note eq 1) to give biradical **2** which then rearranges by radical elimination and reclosure.



The evidence available at that time suggested that the multiplicity of the excited-state species responsible for this transformation, *i.e.*, singlet or triplet, varied from one di-π-methane system to another. Where evidence on the multiplicity was available, the bicyclic examples[2,3,14-18] all appeared to be triplet reactions while the monocyclic and acyclic aryl–vinyl examples[8-10] seemed to be singlet processes.

There was an apparent lack of cases of liquid phase mechanistic and multiplicity studies of acyclic molecules with π systems consisting only of vinyl and without an aryl group.[19] We initiated the study of the photochemistry of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-penta-

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[1] For paper XL of this series, note H. E. Zimmerman and W. R. Elser, *J. Amer. Chem. Soc.*, **90**, 887 (1968).

[2] H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967), reported the rearrangement of barrelene to semibullvalene.

[3] H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 4191 (1968), noted the transformation of benzobarrelene to benzosemibullvalene; see also H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 6096 (1968).

[4] Other examples (see ref 5) are the rearrangement of *trans*-1,3-diphenylpropene to *cis*- and *trans*-1,2-diphenylcyclopropanes[6] and of 3,3,3-triphenylpropene to 1,1,2-triphenylcyclopropane,[7] the transformation of 1,1,3-triphenylindene to 1,2,3-triphenylindene,[7] the photorearrangement of 1-methylene-4,4-diphenyl-2-cyclohexene to *cis*- and *trans*-1,6-diphenyl-4-methylenebicyclo[3.1.0]hexanes,[8] the isomerization of 1-methylene-4,4-diphenylcyclohexa-2,5-diene to *trans*-1,6-diphenyl-4-methylenebicyclo[3.1.0]hex-2-ene,[9] the conversion of various 5-phenyl-1,3-pentadienes to their corresponding 1-phenyl-2-vinylcyclopropanes,[10] the rearrangement of 3,3-dimethyl-1,4,6-heptatriene to the isomeric *cis*- and *trans*-1,1-dimethyl-2,3-divinylcyclopropanes,[11] the transformation of bicyclo[4.2.2]-2,4,7,9-decatetraene to bullvalene,[12] the photorearrangement of dehydroergosteryl acetate to photodehydroergosteryl acetate,[13] the conversion of 2,3-bis(perfluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene to three bis(perfluoromethyl)semibullvalenes,[14] the photochemical rearrangement of benzonorbornadine to 2,3-benzotricyclo[6.1.0^{1,6}.0^{6,7}]-2-heptene,[15] the isomerization of tetrafluorobenzobarrelene to tetrafluorobenzosemibullvalene,[16] the conversion of several dibenzobarrelenes to their corresponding dibenzosemibullvalenes,[17] and the conversion of bicyclo[3.2.1]octa-2,6-diene to tricyclo[3.2.1.0^{1,6}]-4-octene and tricyclo[4.1.1.0^{2,7}]-2-octene.[18]

[5] The first example of an aryl to double bond migration is the case of 4,4-diphenylcyclohex-2-en-1-one studied by H. E. Zimmerman and J. W. Wilson, *J. Amer. Chem. Soc.*, **86**, 4036 (1964). However, the present paper deals only with hydrocarbon examples.

[6] G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *ibid.*, **87**, 1410 (1965).

[7] G. W. Griffin, A. F. Marcantonio, and H. Kristinsson, *Tetrahedron Lett.*, 2951 (1965).

[8] H. E. Zimmerman and G. E. Samuelson, *J. Amer. Chem. Soc.*, **89**, 5971 (1967).

[9] H. E. Zimmerman, P. Hackett, D. F. Juers, and B. Schröder, *ibid.*, **89**, 5973 (1967).

[10] H. Kristinsson and G. S. Hammond, *ibid.*, **89**, 5969 (1967).

[11] W. R. Roth and B. Peltzer, *Ann. Chem.*, **685**, 56 (1965).

[12] M. Jones and L. T. Scott, *J. Amer. Chem. Soc.*, **89**, 150 (1967).

[13] (a) D. H. R. Barton and A. S. Kende, *J. Chem. Soc.*, 688 (1958); (b) D. H. R. Barton, R. Bernasconi, and J. Klein, *ibid.*, 511 (1960).

[14] R. S. H. Liu, *J. Amer. Chem. Soc.*, **90**, 215 (1968).

[15] J. R. Edman, *ibid.*, **88**, 3454 (1966).

[16] J. P. N. Brewer and H. Heaney, *Chem. Commun.*, 811 (1967).

[17] (a) E. Ciganeck, *J. Amer. Chem. Soc.*, **88**, 2882 (1966); (b) P. W. Rabideau, J. B. Hamilton, and L. Friedman, *ibid.*, **90**, 4465 (1968).

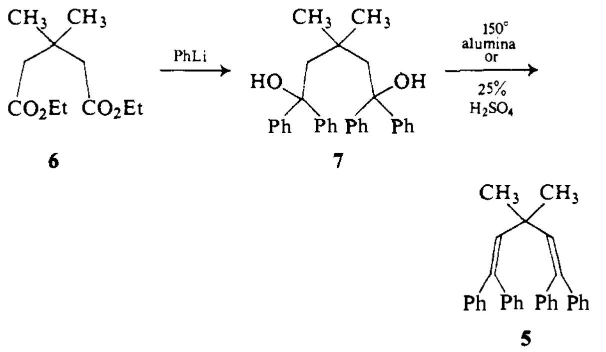
[18] R. R. Sauers and A. Shurpik, *J. Org. Chem.*, **33**, 799 (1968).

[19] In fact, only one liquid phase example of the rearrangement was known, this being Roth's photoisomerization of 3,3-dimethyl-1,4,6-heptatriene.[11] However, in gas phase photochemistry, the mercury-photosensitized rearrangement of several divinylmethane systems was known.[20]

[20] (a) R. Srinivasan and K. H. Carlough, *J. Amer. Chem. Soc.*, **89**, 4932 (1967); J. Meinwald and G. W. Smith, *ibid.*, **89**, 4923 (1967); (c) W. Reusch and D. W. Frey, *Tetrahedron Lett.*, 5193 (1967).

diene (5) in order to determine if the rearrangement would be general for acyclic divinylmethane systems and, if so, to investigate the over-all nature of the reaction. This divinylmethane was selected since it combined the advantages of light absorption in the accessible ultraviolet with the lack of complicating stereochemistry.

Synthesis of the Acyclic Diene. 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene (5), required for the present study, was prepared by the dehydration of 1,1,5,5-tetraphenyl-3,3-dimethylpentane-1,5-diol (7)[21] by heating with alumina or treatment with refluxing 20% sulfuric acid (note eq 2). The structural assignment to 5 and the absence of rearrangement in its preparation was confirmed by the nmr spectrum which showed the presence of two equivalent methyl groups (τ 8.98) and two uncoupled and equivalent vinyl hydrogens (τ 4.05) and by the ultraviolet spectrum (cyclohexane, max 252 nm (ε 23,700)) which is typical of 1,1-diphenylethylenes.



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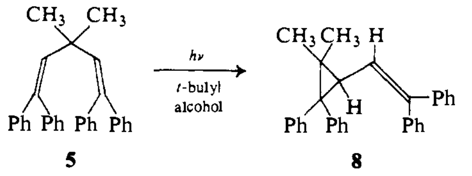
Exploratory Efforts. Irradiation of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (5) in *t*-butyl alcohol (Vycor filter, λ >230 nm) in preparative apparatus (see Experimental Section) afforded a major initial photoproduct 8, mp 139.5–141.0°, and several minor secondary photoproducts (eq 3). The minor products were shown to arise from secondary irradiation of the major product 8; thus, the yield of the major product (8) varied inversely with the extent conversion (*vide infra*). Also, irradiation of 8 produced the same distribution of the minor photoproducts (*vide infra*).

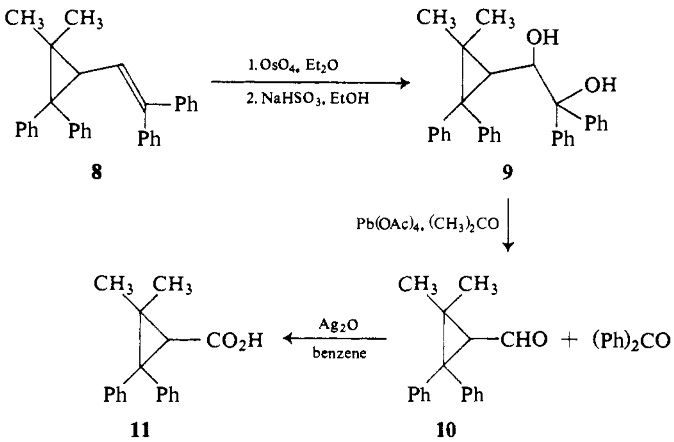


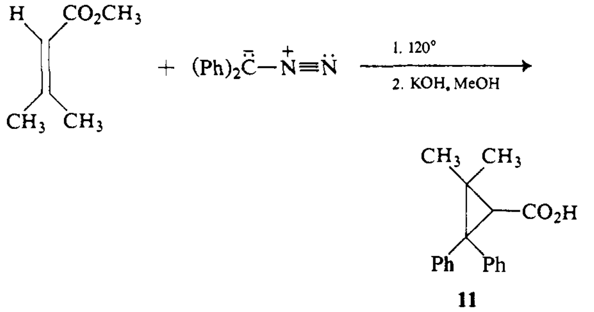
(3)

The structure of photoproduct 8 was determined by spectral and degradative means. The nmr spectrum of 8 showed 20 aromatic hydrogens (τ 2.60–2.85), two nonequivalent methyls (τ 8.70 and 9.01), and an allylic methine (τ 7.84) coupled with a vinyl hydrogen (τ 4.25), J = 10.5 cps. This together with the ultraviolet spectrum (max 271 nm (ε 16,400)), suggested 1,1-diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane as the structure of 8.

An unambiguous structure proof was obtained by the degradation outlined in Chart I. Treatment of the vinylcyclopropane 8 with osmium tetroxide in ether followed by lead tetraacetate oxidation of the glycol 9 yielded the cyclopropyl aldehyde 10, mp 205–208°, and benzophenone. The aldehyde 10 was then oxidized with silver oxide; the product obtained was shown to be 1,1-diphenyl-2,2-dimethylcyclopropyl-3-carboxylic acid (11) by comparison with independently synthesized material.

Chart I. Chemical Degradation of 1,1-Diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane





(4)

The previously unknown 1,1-diphenyl-2,2-dimethylcyclopropyl-3-carboxylic acid (11) was obtained by the reaction of diphenyldiazomethane with methyl 3,3-dimethylacrylate at 135° followed by saponification (note eq 4). This compound had infrared and nmr spectra and a melting point which were identical with those of the material obtained from the degradation of vinylcyclopropane 8.

Multiplicity Studies and Results. Having established the structure of the initial photoproduct of diene 5, we initiated an investigation of the mechanistic details of the reaction.

The first matter attacked was the determination of the quantum yield of the reaction on direct irradiation. As demonstrated in previous investigations,[1,22] the use of isotope dilution analysis is a powerful tool for the determination of quantum yields when low conversions are required. Application of this technique in the present investigation required the preparation of radioactive 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (5). A convenient and useful method for incorporation of

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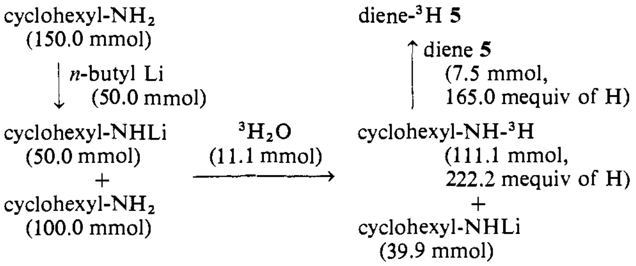
(21) G. Wittig and B. Overman, *Ber.*, **67B**, 2053 (1934).

(22) (a) H. E. Zimmerman and K. G. Hancock, *J. Amer. Chem. Soc.*, **90**, 3749 (1968); (b) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *ibid.*, **90**, 4892 (1968); (c) H. E. Zimmerman and N. Lewin, *ibid.*, **90**, 879 (1968).

tritium into unsaturated and aromatic hydrocarbons was found in a variation of the deuteration method described by Zimmerman, Givens, and Pagni.[3,23] A solution of lithium cyclohexylamide in cyclohexylamine-^{3}H (10 mCi) was prepared by the addition of tritium oxide to excess lithium cyclohexylamide in cyclohexylamine. Treatment of 3.0 g of the diene **5** with fivefold excess of this base at 95° gave 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene-^{3}H containing 2.184 mCi of incorporated tritium. This is an incorporation efficiency of 21.84% based on the total amount of labeled cyclohexylamine. Thus, the tritiation method (Chart II) proved to be quite efficient.

Chart II. Synthesis of Tritium-Labeled 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene



Isotope dilution quantum yield determination of the photochemical isomerization of diene **5** to vinylcyclopropane **8** in cyclohexane at 250 nm revealed an efficiency of 0.0797 ± 0.0032. These results are summarized in Table I.

Table I. Quantum Yields in the Direct Irradiation of 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene

Run[a]	Concn of diene, *M*	Light, mEinstein	Quantum yields, mmol/mEinstein,[b] vinylcyclopropane[c]
1	0.0046	0.038	0.0782 (±0.0031)
2	0.0049	0.044	0.0811 (±0.0032)

[a] In cyclohexane at 250 nm, 24.0°, high intensity monochromator, liquid scintillation analysis. [b] Estimated probable error. [c] Appearance of 1,1-diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane.

In order to determine the multiplicity of the divinylmethane rearrangement of **5**, sensitization studies using isotope dilution were initiated. Photosensitized quantum yields were determined employing sensitizers with varying triplet energies (see Table II). The quantum efficiency of benzophenone (E_T = 68.8 kcal/mol) sensitization of the diene **5** to vinylcyclopropane **8** transformation using conditions under which the ketone absorbed 99% of the light was found to be extremely low (0.0047).

Photosensitization with propiophenone (E_T = 74.6 kcal/mol)[24] was more efficient (*i.e.*, 0.0103) than with benzophenone, but the quantum efficiency was still only *ca.* 13% of that on direct irradiation (see Table II). Chlorobenzene (E_T = *ca.* 82 kcal/mol),[25] of even higher triplet energy, sensitized the divinylmethane rearrangement with the same efficiency (*i.e.*, 0.0096) as propiophenone. In the case of chlorobenzene only 93% of the light was captured by sensitizer and integrated-effective extinction coefficients[26] were used (see Experimental Section).

In view of the surprising inefficiency of the sensitized quantum yields, it was necessary to determine whether we were dealing with ineffective energy transfer or, instead, with a low quantum yield of the triplet process. Four runs were carried out under nearly the same conditions to determine the effectiveness of the energy-transfer process using benzophenone, the lowest energy sensitizer employed above. In the first run, 0.0018 *M* diene **5** was irradiated for a fixed time (*ca.* 21% conversion) giving the usual vinylcyclopropane **8** product. In the second run, a fourfold increase in the time of irradiation and addition of a sufficient quantity of benzophenone to absorb greater than 99% of the light were employed in order to maximize conditions for energy transfer. In this run, starting material (diene **5**) was isolated quantitatively. This is not surprising in view of the low sensitized quantum efficiency found above. In the third run, benzophenone, without any added 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**5**) present, was irradiated in the presence of added benzhydrol. Here, as expected,[27] benzophenone underwent its triplet hydrogen-abstraction reaction to form benzpinacol. Finally, in the fourth run, run 3 was repeated with 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**5**) present. In this run the benzpinacol production was drastically decreased demonstrating energy transfer from benzophenone to diene **5** (*i.e.*, quenching by the diene), and no 1,1-diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane (**8**) was detectable. The design of this run was such that extensive energy transfer could be established, but not the precise efficiency. The results of these four runs are summarized in Table III.

Thus, in runs one and two it was demonstrated that a quantity of light, much greater than the amount capable of effecting appreciable conversion of diene **5** to vinylcyclopropane **8**, when absorbed by benzophenone, was ineffective in photosensitizing the divinylmethane rearrangement. Furthermore, in runs 3 and 4 it was shown that under the sensitization conditions triplet energy transfer from benzophenone to 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**5**) is occurring with modest efficiency.

Interpretive Discussion. Multiplicity of the Rearrangement. The photochemical isomerization of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**5**) to 1,1-diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane (**8**) conclusively demonstrates that the divinyl version of the di-π-methane rearrangement does indeed proceed in acyclic systems. Furthermore, the reaction is one of modest efficiency.

The mechanism of both the sensitized and the direct irradiation are of interest and are considered in this order below.

The low quantum yields on triplet sensitization provide

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(23) A general method of deuterium removal employing lithuim cyclohexylamide is given by Streitwieser and Langworthy (*J. Amer. Chem. Soc.*, **85**, 1757 (1963); our procedure was patterned after this approach.

(24) W. G. Herkltroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(25) S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, **46**, 507 (1964).

(26) Note ref 22b. These take into account the wavelength dependence of the light source and the optical densities of the components competing for light.

(27) G. S. Hammond, *et al.*, *ibid.*, **83**, 2789 (1961).

Table II. Quantum Yields in Sensitized Irradiation of 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene

Run[a]	Concn of diene, *M*	Light, mEinstein	Sensitizer, concn, *M* (E_T, kcal/mol)	Quantum yields, mmol/mEinstein,[b] vinylcyclopropane[c]
3	0.0025	0.186	Benzophenone, 0.280 (68.8)[d]	0.0047 (±0.0002)
4	0.0038	0.308	Propiophenone, 0.407 (74.6)[d]	0.0103 (±0.0004)
5	0.0025	0.081	Chlorobenzene, 7.410 (82.0)[e]	0.0096 (±0.0004)

[a] In cyclohexane at 24.0°. [b] Estimated probable error. [c] Appearance of 1,1-diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane. [d] 313-nm irradiation, sensitizer concentration adjusted to absorb >99% of incident light. [e] 262-nm irradiation.

Table III. Test of Energy Transfer from Benzophenone Triplet to 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene

Run[a]	Time, hr	Wt, g (concn, *M*), of diene **5**	Wt, g (concn, *M*), of benzophenone	Wt, g (concn, *M*), of benzhydrol	Wt, g (%), of benzophenone recovered	Wt, g, of benzpinacol produced	Wt, g, of vinylcyclopropane formed
1	1.0	0.500 (0.0018)	...	...	...	...	0.105
2	4.0	0.500 (0.0018)	4.000 (0.031)	...	2.951 (74.0)	0.824	0.000
3	1.0	... ...	6.000 (0.047)	2.000 (0.015)	1.404 (23.4)	5.851	...
4[b]	1.0	0.500 (0.0018)	6.000 (0.047)	2.000 (0.015)	5.211 (86.8)	0.890	0.000

[a] Irradiation carried out in preparative apparatus, using Pyrex filter in runs 2–4 and Vycor filter in run 1, and *t*-butyl alcohol solvent. [b] Corrected to give product per 1.0-hr irradiation.

evidence on the first point. Triplet energy transfer from benzophenone to diene **5**, shown above by inhibition of the benzophenone photoreduction on addition of diene **5**, is reasonable in view of the relative triplet energies of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene and benzophenone.[28] However, the triplet of diene **5**, once produced, appears to undergo the divinylmethane rearrangement with extremely low efficiency compared to that of the direct irradiation. Nevertheless, the presence of the asymptotic behavior of the efficiency on proceeding from benzophenone (E_T = 68.8 kcal/mol) to propiophenone (E_T = 74.6 kcal/mol) to chlorobenzene (E_T = 82 kcal/mol)[31] sensitization suggests that a finite but inefficient divinylmethane rearrangement is occurring *via* a low energy triplet (*i.e.*, T_1, *vide infra*) in the sensitized runs.

T_2 seems to be precluded as the reacting state in the sensitized irradiation of diene **5** by the observation of the insensitivity of the photosensitized quantum yield to changes in sensitizer triplet energy from 74.6 kcal/mol (propiophenone) to 82 kcal/mol (chlorobenzene). Usually, the efficiency of triplet energy transfer and thus the efficiency of a sensitized reaction increases as the triplet energy of the sensitizer increases to that of the acceptor.[32] We therefore conclude that energy transfer is already perfectly efficient with the 74.6-kcal/mol propiophenone donor, and that there is no transfer to a higher energy and reactive triplet.

Because of the low efficiency of rearrangement of T_1, as determined from the sensitized runs, this excited state cannot be heavily responsible for the rearrangement resulting from direct irradiation. The possibility of an upper triplet (T_2), higher in energy than 82 kcal/mol, being responsible for the direct (*i.e.*, unsensitized) irradiation runs cannot be rigorously excluded. However, if T_2 were the reacting species, it would have to lie between *ca.* 100 kcal/mol and *ca.* 82 kcal/mol in order for it to be accessible from the excited singlet state of diene **5** (E_S = *ca.* 100 kcal/mol) and not be populated in the chlorobenzene (E_T = 82 kcal/mol) sensitized irradiation. This seems not to be the case if we assume that the difference in energy between T_1 and T_2 is in the range of those found by McClure[33] for several condensed ring aromatic systems (*i.e.*, *ca.* 64 kcal/mol), since the energy of a T_2 state of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**5**) would then be *ca.* 120 kcal/mol and of higher energy than the 100 kcal/mol available.

Thus, having excluded triplet states as appreciable participants in the direct irradiation, we are led to conclude that the excited singlet state is the major reacting state of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**5**) in the divinylmethane rearrangement to 1,1-diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane (**8**). This means that the present acyclic divinylmethane utilizes the same multiplicity as the acyclic (*e.g.*, 1,1-dimethyl-1-

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(28) The lowest triplet state of diene **5** should be nearly the same or slightly lower in energy than that of styrene which was found by Evans[29] and Hammond[30] to be at 62 kcal/mol.

(29) D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

(30) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(31) The possibility considered by Zimmerman, Hancock, and Licke[22b] that chlorobenzene, when used as solvent, might transfer singlet energy can now be excluded on the basis of our results. If singlet energy transfer from neat chlorobenzene were taking place, due to exciton transfer with the rate of energy transfer being faster than the rate of diffusion, we would have expected to observe a sensitized reaction of the same efficiency as on direct irradiation, regardless of the multiplicity of the reacting state. Furthermore, the identity of the propiophenone and chlorobenzene sensitization efficiencies also implies that chlorobenzene is triplet sensitizing, since propiophenone is a known useful triplet sensitizer[26] under the concentration conditions used. This adds chlorobenzene to the list of useful triplet sensitizers. Prolonged irradiation does liberate HCl and chlorobenzene must be used in low conversion runs.

(32) (a) H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, **18**, 2355 (1964); (b) G. S. Hammond and W. G. Herkstroeter, *J. Amer. Chem. Soc.*, **88**, 4769 (1966); (c) G. S. Hammond and J. Saltiel, *ibid.*, **84**, 4983 (1962); (d) G. S. Hammond, *et al.*, *ibid.*, **86**, 3197 (1964); (e) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

(33) Employing triplet–triplet absorption studies, McClure[34] found differences in energy between T_1 and T_2 to be *ca.* 68 kcal/mol for naphthalene, *ca.* 67 kcal/mol for anthracene, and *ca.* 58 kcal/mol for phenanthrene. However, for a smaller difference in energy (*ca.* 32 kcal/mol) between T_1 and T_2 note the work of Kellogg.[35]

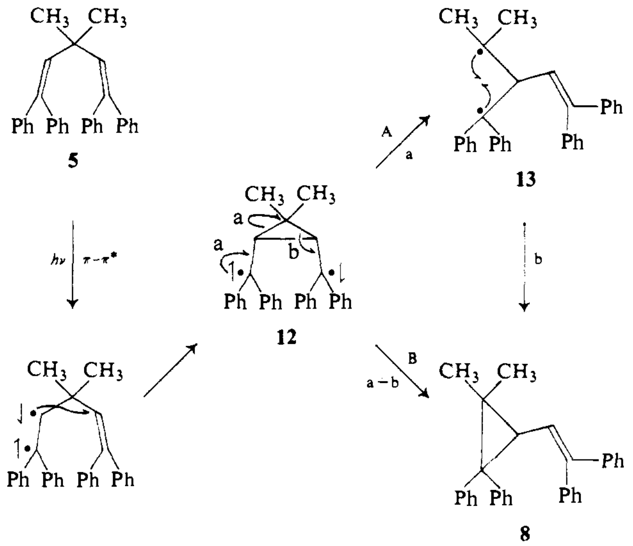
(34) D. S. McClure, *J. Chem. Phys.*, **19**, 670 (1951).

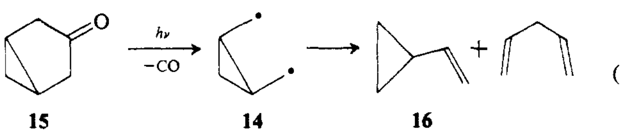
(35) R. Kellogg, *ibid.*, **44**, 411 (1966).

phenyl-5,5-dimethyl-2,4-pentadiene)[10] and monocyclic (*e.g.*, 1-methylene-4,4-diphenyl-2-cyclohexene)[8] arylvinylmethane reaction, but differs from the bicyclic arylvinylmethane (*e.g.*, benzonorbornadiene)[15] and divinylmethane (*e.g.*, barrelene)[2] cases.

Interpretive Discussion. The Reaction Mechanism. The mechanism of the rearrangement of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**5**) to 1,1-diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane (**8**) can be formally depicted as in Chart III. Biradical **12**, formed initially by 2,4 bonding of the π–π* singlet state of 1,4-diene **5**, can proceed to vinylcyclopropane **8** either *via* biradical **13** (path A) or in a concerted manner (path B). Interestingly, a biradical, **14**, quite similar to **12**, formed in the vapor phase decarbonylation of bicyclo-[3.1.0]hexan-3-one (**15**), undergoes the corresponding process to form vinylcyclopropane (**16**) (note eq 5).[36]

Chart III. The Formal Mechanism of the Transformation of 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene to 1,1-Diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane





(5)

From a more sophisticated perspective, the divinylmethane rearrangement of **5**, or for that matter all singlet di-π-methane rearrangements, may in principle proceed in a completely concerted manner. This pathway (see Chart IV) would structurally involve simultaneous cleavage of bond 2–3 and formation of bonds 2–4 and 3–5 with inversion of configuration at C-3. The halfway stage **17** for this transformation consists of a monocyclic array of six orbitals with one sign inversion, and thus is Möbius-like. The delocalized system contains six electrons. Using Zimmerman's Hückel–Möbius mnemonic,[37] the reaction is seen to be allowed in the excited state.[38]

As mentioned briefly above, there appears to be a pattern to the behavior of the photochemistry of di-π-methane systems in which geometry seems to govern the multiplicity of the excited state taking part in the transformation (see Table IV). The bicyclic di-π-methane systems follow the rearrangement pathway efficiently from their excited triplet states, while their excited singlets give rise to different reactions.[2,3,14–18] In contrast, the monocyclic and acyclic di-π-methanes seem to undergo the reaction efficiently only from their excited singlet states.[8–10]

Table IV. The Relationship between Structure and Multiplicity of the Di-π-methane and the Efficiency of the Rearrangement

	Acyclic and monocyclic di-π-methanes	Bicyclic di-π-methanes
Singlet excited state	Efficient	Inefficient
Triplet excited state	Inefficient	Efficient

It may be premature to attempt an explanation of this behavior because of the limited number of examples. However, several factors which may influence this relationship between di-π-methane structure and multiplicity are: (a) acyclic and monocyclic singlet di-π-methanes can rearrange in a concerted manner by way of the Möbius cycle (*vide supra*) without difficulty; (b) the acyclic and monocyclic triplets can dissipate energy by twisting about the double bonds (*i.e.*, leading to a nonvertical excited state) and therefore render themselves unreactive; this assumes twisting only in the triplet state and not in the singlet excited state;[42] (c) bicyclic singlets require considerable strain for effective overlap to give the Möbius

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(36) L. D. Hess and J. N. Pitts, *J. Amer. Chem. Soc.*, **89**, 1973 (1967).

(37) H. E. Zimmerman, *ibid.*, **88**, 1564, 1566 (1966).

(38) (a) From still another perspective the completely concerted process can be visualized as a *trans* addition of single bond 2–3 to π bond 4–5 (*i.e.*, the plus lobe of the sp^2 orbital at C-2 overlapping with the plus lobe of the p orbital at C-4 concerted with the negative lobe of the sp^2 orbital at C-3 overlapping with the negative lobe of the p orbital at C-5 (*cf.* ref 39); note **17′** in Chart IV. The halfway stage of this process would consist of a monocyclic array of four orbitals with no sign inversions, containing four electrons, and thus is Hückel-like and allowed in the excited state.[37] (b) However, this is a rather limited way of picturing the di-π-methane transformation, since the second π bond (*i.e.*, π bond 1–2) seems to be a requisite part of the system in order for the reaction to proceed. (c) Exceptions to the need for the second π bond are Griffin's example of the photochemically induced methyl migration in 1-phenyl-3,3-dimethylbutene,[40] and the photoisomerization of 4-alkylcyclohexenones to bicyclic ketones.[41] But in general, the efficiencies of the apparent exceptions are low (*e.g.*, see ref 41b), demonstrating the role of the second π bond.

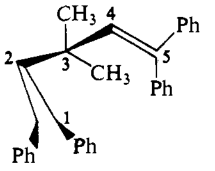
(39) Actually, the divinylmethane stereochemistry has been discussed from this viewpoint by Hoffman (Reaction Mechanisms Conference, Brandeis University, Waltham, Mass., June 1968) and this treatment does lead to the same prediction of inversion of configuration at C-3 (*vide supra*). It should be noted that the 2A + 2A designation for this four-orbital process can be derived directly from Hückel–Möbius considerations since the 2A + 2A reaction involves an even or zero number of sign inversions which is Hückel-like. More general, this treatment is identical with the previously mentioned Möbius–Hückel approach[37] except that the orbitals are taken in pairs rather than singly. For each 2A interaction one sign inversion is introduced into the cyclic array of orbitals. With an odd number of inversions, a Möbius species results (favoring $4n$ electrons in the ground and $4n + 2$ in the excited state). With an even number of inversions a Hückel system is formed with the reverse demands.

(40) H. Kristinsson and G. W. Griffin, *J. Amer. Chem. Soc.*, **88**, 378 (1966).

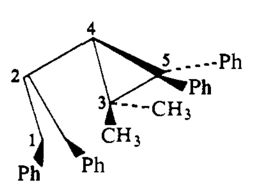
(41) (a) W. W. Kwie, B. A. Shoulders, and P. D. Gardner, *ibid.*, **84**, 2268 (1962); (b) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *ibid.*, **88**, 1965 (1966); (c) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fritton, *Tetrahedron Lett.*, 2049 (1963).

(42) Photoisomerization of olefins which results from twisting about the double bond appears to be, exclusively, a triplet excited state process.[43]

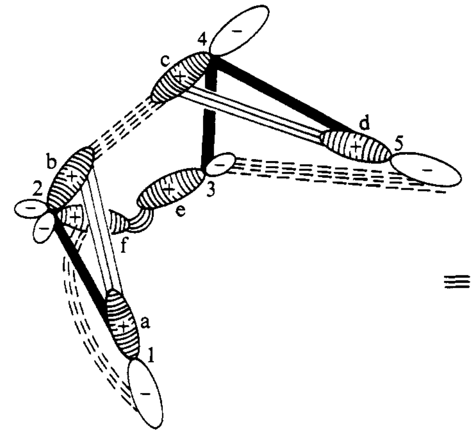
Chart IV. Halfway Stage in the Concerted Divinylmethane Rearrangement



5

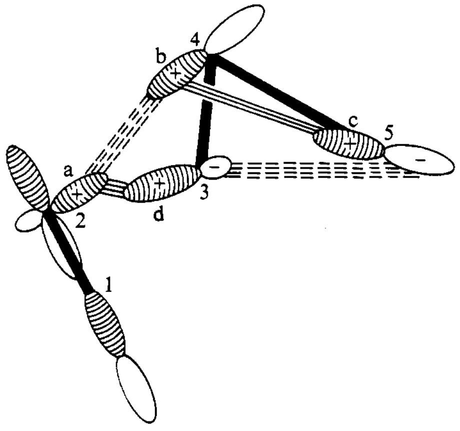


8



17

≡



17′

ordering in cyclic array (**17**)		
a–b	+ +	one sign discontinuity
b–c	+ +	
c–d	+ +	
d–e	− −	
e–f	+ +	
f–a	+ −	

ordering in cyclic array (**17′**)		
a–b	+ +	zero sign discontinuity
b–c	+ +	
c–d	− −	
d–a	+ +	

≡≡≡ bonds forming ≡ bonds breaking ▬ bonds unchanged

cycle and thus may not be able to undergo the reaction in a concerted fashion; (d) bicyclic triplet di-π-methanes are not able to dissipate their energy by twisting about the double bonds and their reacting centers are held together by the rigidity of the system; the bicyclic di-π-methanes appear to react nonconcertedly.[2,3]

Experimental Section[44]

Diethyl 3,3-Dimethylglutarate. This was prepared by a slight modification of the method of Reid and Gompf[45] in an 85% yield starting with 3,3-dimethylglutaric acid (Aldrich).

1,1,5,5-Tetraphenyl-3,3-dimethylpentane-1,5-diol.[21] To a solution of 1.33 mol of phenyllithium, prepared from 212.00 g (1.33 mol) of bromobenzene and 19.80 g (2.83 g-atoms) of freshly cut lithium, in 250 ml of anhydrous ether was added a solution of 53.49 g (0.25 mol) of diethyl 3,3-dimethylglutarate in 200 ml of anhydrous ether dropwise over a period of 1.0 hr with cooling when necessary. The resulting mixture was refluxed for 48 hr and quenched with 150 ml of water. The ether layer was separated, washed with water, dried, and concentrated *in vacuo* yielding 106.20 g of a tacky solid. This material was taken up in hot hexane–ether and upon cooling gave 32.60 g (30.1%) of a white crystalline solid, mp 158.0–161.0°, identified as 1,1,5,5-tetraphenyl-3,3-dimethyl-1,5-pentanediol. A small quantity of this material was recrystallized from hexane–ether to a constant melting point of 162.5–163.0° (lit.[21] 156–157°).

The spectral data were as follows: infrared (CS_2) 2.92 (sh), 8.0–9.0 (br) 12.95, 13.46, and 14.30 μ; nmr ($CDCl_3$) τ 2.4–3.1 multiplet (20 H, aromatic), 5.98 singlet (2 H, hydroxyl), 7.32 singlet (4 H, methylene), and 9.55 singlet (6 H, methyl).

Anal. Calcd for $C_{31}H_{32}O_2$: C, 85.27; H, 7.40. Found: C, 84.97; H, 7.27.

1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene. Alumina Pyrolysis of 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,5-pentanediol. A homogeneous mixture of 0.50 g (1.14 mmol) of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,5-pentanediol and 1.00 g of alumina (Woelm, activity grade 1) was heated at 180° for 0.75 hr. After cooling to room temperature the residue was ether extracted; the extracts were filtered and concentrated *in vacuo* to give 0.43 g of a crystallizing oil which was subjected to chromatography on a 3.0 × 30.0 cm column, slurry packed with silica gel (Davison grade 950, 60–200 mesh) in hexane. Elution was with 3.0 l. of 3% ether–hexane; 200-ml fractions were collected. Fractions 4–10 gave 0.399 g of a white crystalline solid. Recrystallization from hexane gave 0.260 g (56.7%) of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene, mp 110.0–111.5°.

The spectral data for this compound were as follows: infrared ($CHCl_3$) 3.25, 3.31, 3.37, 3.49, 6.28, 6.92, 7.35, 8.49, 8.85, 9.31, 9.70, 11.30, and 14.40 μ; nmr ($CDCl_3$) τ 2.81–3.00 multiplet (20 H, aromatic), 4.05 singlet (2 H, vinyl), 8.98 singlet (6 H, methyl); ultraviolet (cyclohexane) max 252 nm (ε 23,700).

Anal. Calcd for $C_{31}H_{28}$: C, 92.94; H, 7.06. Found: C, 93.09; H, 6.98.

1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene. Sulfuric Acid

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(43) (a) R. F. Borkman and D. R. Kearns, *J. Amer. Chem. Soc.*, **88**, 3467 (1966); (b) G. S. Hammond and W. M. Moore, *ibid.*, **81**, 6334 (1959); (c) J. Saltiel and G. S. Hammond, *ibid.*, **85**, 2515 (1963); (d) note also ref 10 and 30.

(44) All melting points were taken on a hot-stage apparatus checked with known compounds.

(45) E. B. Reid and T. E. Gompf, *J. Org. Chem.*, **18**, 661 (1953).

Dehydration. A mixture of 1.58 g (3.62 mmol) of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,5-pentanediol, 17 ml of 20% sulfuric acid, and 17 ml of *p*-dioxane was refluxed at 110° for 4 hr. After cooling, 50 ml of ether was added and the ethereal layer separated, washed successively with 5% sodium hydroxide and water, dried, and concentrated *in vacuo* giving 1.65 g of an oil. This crude material was chromatographed on a 3.0 × 66 cm column slurry packed with silica gel (Davison grade 950, 60–200 mesh) in hexane. Elution was with 5 l. of hexane and 2 l. of 1% ether–hexane; 250-ml fractions were collected. Fractions 7–21 gave 520 mg of a crystallizing oil which after recrystallization from hexane yielded 431 mg (29.8%) of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene, mp 110.0–111.5°. The spectral data were the same as that of the diene obtained from alumina dehydration of the corresponding diol.

Photolysis of 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene. A solution of 3.00 g (7.50 mmol) of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene in 1 l. of *t*-butyl alcohol was purged with purified[46] nitrogen for 1.0 hr before, and then during the photolysis. The irradiation was carried out using a 450-W Hanovia medium-pressure lamp with Vycor glass filter, all in a water-cooled immersion well for 3.0 hr. The progress of the reaction was monitored by examining the uv spectra of aliquots. Solvent removal *in vacuo* gave 3.152 g of slightly yellow oil which was subjected to liquid–liquid partition chromatography on a 3 × 204 cm column, slurry packed with polystyrene beads[47] (Dow X2, 2% crosslinked, 100–200 mesh). The beads were thoroughly washed with chloroform, dried, and soaked in the cyclohexane enriched upper phase of a 1:1 cyclohexane–methanol mixture and slurry packed in the methanol-enriched lower phase of the 1:1 cyclohexane–methanol. Elution was with the lower phase and 20-ml fractions were collected with scanning of the eluent absorbance at 260 nm.

Four peaks were observed in the scan: fractions 26–43, 0.025 g of a noncrystallizing oil; 90–115, 0.189 g of what was later identified as secondary photoproduct A; 116–123, 0.066 g of overlap; 124–170, 0.902 g of essentially pure 1,1-diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane as a slightly yellow crystallizing oil; 171–180, 0.181 g of overlap; 181–231, 1.557 g of a mixture of starting diene and secondary photoproducts B, C, and D.

The vinylcyclopropane obtained above (0.902 g) was purified by recrystallization from 95% ethanol giving 0.637 g of a white crystalline solid, mp 139–141.5°. The spectral data were as follows: ir (CS_2) 3.23, 3.26, 3.30, 3.40, 6.28, 6.71, 6.93, 7.24 (doublet), 7.50, 8.55, 8.87, 8.98, 9.32, 9.67, 10.08, 13.41, 14.35, and 15.93 μ; nmr ($CDCl_3$) τ 2.60–2.85 multiplet (20 H, aromatic), 4.25 doublet (1 H, $J = 10.5$ cps, vinyl), 7.84 doublet (1 H, $J = 10.5$ cps, cyclopropyl methine), 8.70 singlet (3 H, methyl), 9.01 singlet (3 H, methyl); uv (*t*-butyl alcohol) max 271 nm (ε 24,300).

Anal. Calcd for $C_{31}H_{28}$: C, 92.94; H, 7.06. Found: C, 92.94; H, 7.18.

A white solid was crystallized from fractions 181–231 by addition of hexane giving 0.872 g, mp 105–109°. The nmr spectrum of this material showed it to be 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene. The mother liquors from the above were subjected to preparative layer chromatography on fluorescent silica gel (Brinkman, PF_{254}) using 20 × 20 cm plates. Ten developments with 4% benzene–hexane gave three overlapping bands which were cut and ether extracted. Concentration *in vacuo* of each gave the following: cut 1 (R_f *ca.* 0.75), 0.302 g of a crystallizing oil containing *ca.* 76% starting diene and 24% secondary photoproduct B; cut 2 (R_f *ca.* 0.65), 0.165 g of an oil containing mainly secondary photoproduct C; cut 3 (R_f *ca.* 0.50), 0.203 g of a partially crystallizing oil containing mostly secondary photoproduct D. The identity of unknowns A–D is discussed below in connection with the 1,1-diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane photochemistry.

The total yield of recovered diene was 0.902 g (30.1%) and of pure vinylcyclopropane was 0.637 g (21.2%, 30.4% based on recovered starting material).

Characterization of 1,1-Diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane. Degradation to 1,1-Diphenyl-2,2-dimethyl-3-cyclopropylcarboxaldehyde. A mixture of 432 mg (1.05 mmol) of the vinylcyclopropane photoproduct and 400 mg of osmium tetroxide (1.58 mmole) in 50.0 ml of anhydrous ether was stirred at room temperature for 48 hr. The ether was removed *in vacuo* and the resulting black osmate ester hydrolized by refluxing in a solution of 3.00 g of sodium bisulfite in 50.0 ml of 95% ethanol for 5.0 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 *in vacuo* yielding 465 mg of a clear oil which was shown by nmr and ir to contain the wanted glycol. Purification of this material was not attempted.

The crude glycol (465 mg), 1.50 g of freshly prepared lead tetraacetate, and 1.00 g of sodium acetate were stirred at room temperature in 50 ml of dry acetone for 48 hr. The crude reaction product was filtered and the filtrate diluted with ether, washed with water, dried, and concentrated *in vacuo* giving 453 mg of an oil. This material was chromatographed on a 2 × 70 cm column slurry packed with silica gel (Davison grade 950, 60–200 mesh) in hexane. Elution was with 1 l. of 4% ether–hexane, 2 l. of 6% ether–hexane, and 2 l. of 20% ether–hexane; 250-ml fractions were collected. Fractions 1–5 gave 186 mg of a clear oil, 6–11 gave 219 mg of a white solid, and 13–15 gave 64 mg of a white solid.

Fractions 1–5 after recrystallization (95% ethanol), yielded 95.0 mg of a solid, mp 46–47.5°, which showed nmr and infrared spectra identical with those of an authentic sample of benzophenone (mp 48°).

Fractions 6–11 after recrystallization from hexane yielded 139 mg of a solid, mp 205–208°, characterized as 1,1-diphenyl-2,2-dimethylcyclopropyl-3-carboxaldehyde. The spectral data for this compound were as follows: infrared ($CHCl_3$) 3.25, 3.42, 3.49, 5.93 (cyclopropyl ketone), 6.26, 6.61, 6.70, 8.85, 9.00, and 14.40 μ; nmr ($CDCl_3$) τ 0.88 doublet (1 H, $J = 7.0$ cps, aldehydic), 2.6–2.9 multiplet (10 H, aromatic), 7.72 doublet (1 H, $J = 7.0$ cps, cyclopropyl methine), 8.49 singlet (3 H, methyl), and 8.91 singlet (3 H, methyl).

Fractions 13–15 after recrystallization from benzene-hexane yielded 45 mg of a solid, mp 218–222°, which was later shown to be identical with the cyclopropyl acid obtained by oxidation of the aldehyde (*vide supra*) and by independent synthesis.

Characterization of 1,1-Diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane. Silver Oxide Oxidation of 1,1-Diphenyl-2,2-dimethyl-3-cyclopropylcarboxaldehyde. Moist silver oxide (0.05 mol), freshly prepared from 500 mg of silver nitrate and 9.0 ml of 20% sodium hydroxide, was mixed with 126 mg (0.63 mmol) of 1,1-diphenyl-2,2-dimethyl-3-cyclopropylcarboxaldehyde in 30 ml of benzene and refluxed for 20 hr with stirring. After *ca.* 10 hr a silver mirror formed on the walls of the flask. After cooling, ether was added, and the resulting suspension was filtered. The filtrate was extracted with 20% sodium hydroxide. The dried neutral fraction after concentration *in vacuo* gave 82 mg (65.1%) of a crystallizing oil which by nmr and ir spectra was shown to be unreacted aldehyde.

The basic extract was made acidic to congo red with concentrated hydrochloric acid and ether extracted. The ether extract was washed with water, dried, and concentrated *in vacuo* giving 54 mg of a white crystalline solid. Recrystallization from benzene–hexane gave 45 mg (27.0%), mp 231.0–233.5°. The ir and nmr spectra of this material were identical with the spectra of the synthesized 1,1-diphenyl-2,2-dimethylcyclopropyl-3-carboxylic acid (*vide infra*).

Diphenyldiazomethane. This material was prepared by the method of Miller[48] from benzophenone hydrazone and mercuric oxide.

Methyl 3,3-Dimethylacrylate. This material was synthesized according to the method of Wagner and Moore[49] from 3,3-dimethylacrylic acid (Eastman).

1,1-Diphenyl-2,2-dimethyl-3-cyclopropylcarboxylic Acid. A solution of 15.00 g (0.077 mol) of diphenyldiazomethane in 200 ml of hexane was added dropwise over a 12-hr period to 9.00 g (0.079 mol) of methyl 3,3-dimethylacrylate at 135° with stirring. After cooling, the mixture was added to 20.0 g of potassium hydroxide in 200 ml of methanol and the resulting solution stirred for 24 hr at room temperature. The methanol was then removed *in vacuo* and the remaining tacky solid taken up in water and ether extracted. Concentration of the ether extract after drying gave 8.04 g of a solid, mp 165–170°, whose nmr spectrum showed it to be impure 1,1,2,2-tetraphenylethane.

The aqueous layer was made acidic to congo red with con-

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[46] Purified by vanadous sulfate removal of oxygen by the method of Meites and Meites (*Anal. Chem.*, **20**, 984 (1948)).

[47] We thank the Dow Chemical Co. for kindly supplying polystyrene beads for development of this technique.

[48] J. B. Miller, *J. Org. Chem.*, **24**, 560 (1959).

[49] R. B. Wagner and W. R. Moore, *J. Amer. Chem. Soc.*, **72**, 1964 (1950).

Table V. Photolysis to Varying Conversions of 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene

Run[a]	Time, min	Vinylcyclopropane **8**, mg[b]	Diene **5** recovered, mg[b]	Conversion to vinylcyclopropane 8, %	Yield vinylcyclopropane **8**, %
1	10.0	145	352	28.8	97.3
2	20.0	146	258	29.2	60.3
3	30.0	131	195	27.1	42.9

[a] Photolysis of 500 mg of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene in *t*-butyl alcohol. [b] Based on nmr analysis of crude material after liquid–liquid partition chromatography on polystyrene beads. [c] Based on unrecovered diene.

centrated hydrochloric acid and methylene chloride extracted. The organic extract was dried and concentrated *in vacuo* giving 11.708 g of an oil which was chromatographed on a 3.5 × 115 cm column slurry packed with silica gel (Davison grade 950, 60–200 mesh) in 5% ether–hexane. Elution was with 3 l. of 7%, 2 l. of 10%, 5 l. of 13%, and 2 l. of 16% ether–hexane; 500-ml fractions were collected. Fractions 3–7 gave 1.749 g of a solid identified as 1,1,2,2-tetraphenylethane; 10–24 gave 3.581 g of a semisolid whose nmr showed it to be a mixture of 2,2-dimethylacrylic acid and the wanted cyclopropyl acid. Fractional recrystallization from 1:1 benzene–hexane gave 0.81 g (29.6%) of a white solid, mp 232–234°, which was characterized as 1,1-diphenyl-2,2-dimethylcyclopropyl-3-carboxylic acid.

The spectral data of this compound were as follows: infrared ($CHCl_3$) 3.10–4.20 (br), 5.90 (cyclopropyl acid), 6.26, 6.70, 6.92, 7.00, and 9.00 μ; nmr ($CDCl_3$) τ 1.00 broad singlet (1 H, acid), 2.80 singlet (10 H, aromatic), 7.70 singlet (1 H, methine), 8.50 singlet (3 H, methyl), 8.91 singlet (3 H, methyl).

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.16; H, 6.82. Found: C, 80.98; H, 6.99.

Photolysis of 1,1-Diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane. A solution of 615 mg of 1,1-diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane in 700 ml of *t*-butyl alcohol was irradiated using the same apparatus described above with a Vycor glass filter for 2.0 hr under a nitrogen atmosphere. Concentration *in vacuo* gave 627 mg of a viscous oil. The nmr spectrum of this material showed that no starting vinylcyclopropane remained and was quite similar to the spectrum of the crude material obtained from photolysis of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene minus the vinylcyclopropane. This material was subjected to liquid–liquid partition chromatography on a 3.0 × 204 cm column slurry packed with polystyrene beads (Dow, X2, 2% crosslinked, 100–200 mesh) in the lower phase of 1:1 methanol–cyclohexane. Elution was with lower phase of 1:1 methanol–cyclohexane; 20-ml fractions were collected, and eluent absorbance was scanned at 260 nm.

Four peaks were observed in the scan: fractions 46–86, 49 mg of a noncrystallizing oil, photoproduct E; 87–119, 82 mg of a noncrystallizing oil, photoproduct A; 120–130, 43 mg of overlap; 131–180, 150 mg of a mixture shown by nmr to contain mostly starting vinylcyclopropane; 181–273, 277 mg of a mixture of several products.

Fractions 181–273 were subjected to preparative layer chromatography on silica gel (Brinkman, PF_{254}) using 20 × 20 cm plates. Elution was with 5% benzene–hexane and ten developments were carried out. Three major bands were obtained: cut 1 (R_f *ca.* 0.75), 85 mg of a white solid, mp 138–142°, tentatively designated as photoproduct B; cut 2 (R_f *ca.* 0.65), 93 mg of a viscous oil designated as photoproduct C; cut 3 (R_f *ca.* 0.50), 50 mg of a white solid, mp 157–159°, designated as photoproduct D.

Photoproducts A–D showed identical nmr, ir, and uv spectra as those found on direct irradiation of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene.

Photolysis to Varying Conversions of 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene. Three separate solutions of 500 mg (1.25 mmol) of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene in 500 ml of *t*-butyl alcohol were purged with nitrogen[46] for 1.0 hr before, and during photolysis and were irradiated using the same apparatus described earlier with a Vycor glass filter for 10.0, 20.0, and 30.0 min.

Run 1 (10.0-min irradiation) after concentration *in vacuo* gave 533 mg of a crystalline solid which was subjected to liquid–liquid partition chromatography on a 3.0 × 204 cm column, slurry packed with polystyrene beads (Dow, X2, 2% crosslinked, 100–200 mesh) in the lower phase of 1:1 methanol–cyclohexane. Elution was with the lower phase of 1:1 methanol–cyclohexane; 40-ml fractions were collected, and eluent absorbance was scanned at 260 nm. Fractions 60–71, 7 mg of secondary photoproduct A; 72–97, 145 mg of a crystallizing oil shown by nmr (CCl_4) analysis to contain 99.0 ± 5.0% of 1,1-diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane (10.5:212, ratio of relative areas of vinyl to aromatic protons); 98–127, 372 mg of a crystalline solid shown by nmr (CCl_4) analysis to contain 94.9 ± 5.0% of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (19:210, ratio of relative areas of vinyl to aromatic protons).

Run 2 (20.0-min irradiation) after concentration *in vacuo* gave 543 mg of a partially crystalline solid which was subjected to chromatography on the polystyrene system described above. Fractions 46–66, 25 mg of secondary photoproduct A; 67–92, 135 mg of an oil shown by nmr (CCl_4) analysis to contain 99.0 ± 5% of the vinylcyclopropane (19.5:183.1 ratio of relative areas of vinyl and aromatic protons); 93–96, 22 mg of a mixture found by nmr (CCl_4) analysis to contain *ca.* 50 ± 5% of the starting diene and *ca.* 50 ± 5% of the vinylcyclopropane; 97–128, 325 mg of a semisolid shown by nmr (CCl_4) analysis to contain 76.9 ± 5.0% of the diene (17:221, ratio of relative areas of vinyl to aromatic protons).

Run 3 (30.0-min irradiation) after concentration *in vacuo* gave 570 mg of an oil which was subjected to chromatography on the polystyrene system described above. Fractions 42–65, 54 mg of secondary photoproduct A; 66–91, 124 mg of an oil shown by nmr (CCl_4) analysis to contain 98.0 ± 5.0% of the vinylcyclopropane (12.0:225, ratio of relative areas of vinyl to aromatic protons); 92–95, 14 mg of a mixture of *ca.* 50 ± 5% of the vinylcyclopropane and *ca.* 50 ± 5% of the starting diene; 96–127, 308 mg of an oil shown by nmr (CCl_4) analysis to contain 62.2 ± 5.0% of the diene (12.0:193, ratio of relative areas of vinyl to aromatic protons) (see Table V).

Direct Irradiation of 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene. Control Run. A solution of 500 mg (1.25 mmol) of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene in 700 ml of *t*-butyl alcohol was purged with nitrogen before and then during a 1.0-hr irradiation, run in the same apparatus described above, however with a Vycor filter. After termination of the irradiation the solvent was removed *in vacuo* giving 565 mg of a slightly yellow oil which was then subjected to liquid–liquid partition chromatography on a 3 × 204 cm column packed with polystyrene beads (Dow X2, 2% crosslinked) (*vide supra*). Elution was with the methanol enriched phase of 1:1 cyclohexane–methanol while scanning at 260 nm; 20-ml fractions were collected.

Fractions 141–174 gave 105 mg of a slightly yellow solid whose nmr spectrum showed it to be essentially pure 1,1-diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane. This corresponds to 21% conversion of the diene. Recrystallization of this material gave 54 mg of the vinylcyclopropane, mp 139.5–141.0°.

Benzophenone-Sensitized Photolysis of 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene. A solution of 0.500 g (1.25 mmol) of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene and 4.000 g (21.90 mmol) of benzophenone in 700 ml of *t*-butyl alcohol was purged with purified nitrogen[46] for 1.0 hr before, and during the photolysis. Irradiation was carried out using the same apparatus described above for 4.0 hr, this time employing a Pyrex glass filter (99% of the light absorbed by the ketone). Concentration *in vacuo* gave 5.197 g of a semisolid which was subjected to chromatography on a 3.0 × 100 cm column, slurry packed with silica gel (Davison grade 950) in hexane. Elution was with 1 l. of 5%, 2 l. of 8%, 1.5 l. of 12%, 1.5 l. of 18%, and 2 l. of 35% benzene–hexane, 2 l. of 5%, and 4 l. of 10% ether–hexane with 500-ml fractions being collected. Fractions 12–15 gave 0.487 g of a white solid, mp 101–

109°, identified as essentially pure diene; 20–22 gave 2.951 g of a clear oil identified as benzophenone; 23–27 gave 0.824 g of a white solid, mp 186°, identified as benzpinacol.

The nmr spectrum taken of fractions 12–15 showed the presence of only 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene and no 1,1-diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane.

Test for Energy Transfer to Diene by Benzophenone. Photoreduction of Benzophenone by Benzhydrol. A solution of 6.000 g (33.00 mmol) of benzophenone and 2.000 g (10.9 mmol) of benzhydrol in 700 ml of *t*-butyl alcohol was purged with purified nitrogen[46] for 1.0 hr before, and during the photolysis. Irradiation was carried out using the same apparatus as described above for 2.5 hr using a Pyrex glass filter. Concentration *in vacuo* gave 8.8534 g of a pale yellow solid which was subjected to chromatography on a 3.0 × 100 cm column slurry packed with silica gel (Davison, grade 950) in hexane. Elution was with 4.0 l. of 5% ether–hexane, and 4.5 l. of 10% ether–hexane with 500-ml fractions being collected. Fractions 4–6 gave 0.812 g of a crystallizing clear oil, mp 38–43°, characterized as benzophenone; 7–8 gave 0.769 g of a semisolid which was identified as a mixture of benzophenone (78%) and benzpinacol (23%); 9–17 gave 5.674 g of a crystalline solid, mp 188–190°, characterized as benzpinacol.

Photoreduction of Benzophenone by Benzhydrol with Added 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene. Photolysis of a solution of 6.000 g (33.00 mmol) of benzophenone, 2.000 g (10.90 mmol) of benzhydrol, and 0.500 g (1.25 mmol) of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene employing the exact same conditions as described above (700 ml of *t*-butyl alcohol, Pyrex glass filter, 2.5 hr) gave after concentration *in vacuo* 7.798 g of a partially crystalline oil which was chromatographed on a 3.0 × 100 cm column, slurry packed with silica gel (Davison, grade 950) in hexane. Elution was with 1 l. of 10% benzene–hexane, 4 l. of 18% benzene–hexane, 2 l. of 4%, 4 l. of 7%, 1 l. of 12%, and 2 l. of 40% ether–hexane with 500-ml fractions being collected. Fractions 5–11 gave 0.499 g of a crystalline solid, mp 102–106°, identified as exclusively starting diene; 15–17 gave 4.337 g of a crystallizing oil, mp 37–44°, characterized as benzophenone; 18 gave 0.763 g of a mixture of benzophenone (27%) and benzpinacol (73%); 19–24 gave 1.668 g of a crystalline solid, mp 192–195°, identified as benzpinacol; and 25–28 gave 1.259 g of a white solid, mp 61–65°, characterized as benzhydrol.

Preparation of 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene-^{3}H. To a suspension of 3.000 g (7.50 mmol) of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene in 14.850 g (150.0 mmol) of cyclohexylamine (purified by distillation from calcium hydride) under nitrogen was added 25.0 ml (50.0 mmol) of a 2 *M* hexane solution of *n*-butyllithium and the resulting mixture stirred for 0.5 hr. To this was added 0.20 ml (20 mCi) of tritium dioxide (100 mCi/ml) and the resulting mixture refluxed at 95° for 48 hr. After cooling to room temperature, 20.0 ml of water was added as rapidly as possible. After the addition of ether the mixture was separated and the ethereal layer extracted repeatedly with 5% hydrochloric acid and water, dried, and concentrated *in vacuo* giving 3.105 g of a crystalline solid. Recrystallization from 3:1 95% ethanol–hexane to constant melting point gave 2.009 g, mp 110–112°, of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene.

The mother liquors from above were chromatographed on a 3.0 × 95 cm column, slurry packed with silica gel (Davison grade 950, 60–200 mesh) with hexane. Elution was with 7 l. of 17% benzene–hexane, and 500-ml fractions were collected. Fractions 6–13 gave 0.909 g of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene, mp 108–110°. This material was combined with that from above and recrystallization from 3:1 95% ethanol–hexane to constant activity gave 2.102 g (70.1%), mp 110–111.5°, activity 416.37 µCi/mmol, of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene-^{3}H.

Quantum Yield Equipment. The basic apparatus employed by Zimmerman and Hancock[22] was used. Determinations were carried out on an L-shaped optical bench in quartz-faced,[50] thermostated cells, and with stirring. A 2 × 2 × $^1/_{16}$ in. quartz plate mounted at 45° was used as a beam splitter. Two cells were situated in the main optical path in series (cells 1 and 2) and the third cell was perpendicular to the main path. The light source was an Osram HBO 200-W super-pressure mercury lamp in series with a Bausch and Lomb high-intensity monochromator.

Quantum Yield Irradiations. Each determination involved three runs; run 1 with actinometer solution in all three cells, run 2 with organic reactant in the first cell (cell 1) and actinometer in the other two, and run 3 identical with run 1. In practice, less than 1% of the incident light was transmitted by cell 1. The transmission to reflection ratio of the quartz beam splitter (*ca.* 10:1) was calculated exactly during runs 1 and 3. The quantity of light entering the reaction cell (cell 1) in run 2 was then determined using this ratio and the light output in cell 3. Available light in sensitized runs was corrected, when necessary, for direct absorption of part of the light by reactant.

Ca. 0.005 *M* solutions of radioactive substrates in cyclohexane were irradiated at 24.0° under deoxygenated nitrogen.[46] Ultraviolet spectra recorded before and after photolysis were within 5% of calculated spectra assuming Beer's law. After removal of the solvent *in vacuo* the ^{3}H-photolysate residue was diluted volumetrically. Aliquots were withdrawn volumetrically for isotopic dilution with accurately weighed excesses of pure ^{1}H-photoproduct and starting material. Recrystallization to constant activity was then carried out using 3:1 95% ethanol–hexane.

In sensitized runs, the sensitizer was removed by short-path distillation before dilution except in the case of benzophenone where removal was accomplished by column chromatography on silica gel (Davison grade 950, 60–200 mesh) after dilution.

Potassium Ferrioxalate Actinometry.[51] Potassium ferrioxalate actinometry was employed. Absorbance of the ferrous–phenanthroline complex was measured at 510 nm on a Beckman Model DU spectrometer with Gilford digital absorbance readout. The apparatus was checked[22] at 366 nm with uranyl oxalate actinometry.[52]

Sensitizers. Propiophenone (Pennsylvania Coal Products) was distilled twice, bp 41° (0.15 mm). Benzophenone (Eastman) was recrystallized three times from 95% ethanol, mp 49.0–49.5°. Chlorobenzene (Eastman) was distilled before use.

Specific Activity of ^{3}H Compounds. Assay was accomplished by liquid scintillation counting using a Nuclear-Chicago Mark I scintillation system.

Integrated Extinction Coefficients. In the chlorobenzene-sensitized irradiation of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene, an appreciable quantity of direct absorption of the incident light by the diene over the 22-nm band width employed was present. Wavelength dependence of the extinction coefficients and lamp output made calculated absorbance ratios at 263 nm for chlorobenzene *vs.* diene inaccurate. Integrated extinction coefficients which took into account the above-mentioned wavelength dependences were determined. Light intensity through a high-intensity Bausch and Lomb monochromator (22-nm band width) at 263 nm transmitted through a 10-cm cell filled with cyclohexane, and solutions of diene, and chlorobenzene, alternately, were monitored using a Kettering YSI radiometer. Calculation of extinction coefficients using Beer's law gave average values of 0.38 ± 0.02 for chlorobenzene and 85 ± 5 for 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene.

Quantum Yield Summaries. Specific data for individual determinations are listed as follows: first, condition of irradiation of ^{3}H-labeled reactant (weight, solvent, wavelength, temperature, and amount of light), followed by isotope dilution data. The weight of each ^{1}H compound used to dilute an aliquot of the labeled reaction mixture is followed by the number of the final recrystallization, recovered weight, melting point, asymptotic specific activity (µCi/mmol) with standard error; calculated amount of product produced or starting material recovered; quantum yield. The quantum yield for disappearance of reactant was obtained only as the quantum yield for the appearance of product, since the low conversions made the absolute errors in amounts of reactant consumed and recovered comparable in magnitude to their differences.

Run 1. 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene-^{3}H (71.8 mg, 179.5 µmol), activity 416.37 µCi/mmol in 39.0 ml of cyclohexane irradiated through monochromator (band width 22 nm) at 250 nm and 24°, 37.88 µEinsteins; analysis by liquid scintillation counting.

1,1-Diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane (483.6 mg, 1207 µmol) added to ^{3}H photolysate (64.6 mg, 161.6 µmol): 10, 145 mg, 139.5–41.0°, 0.918 ± 0.008 µCi/mmol; 2.963 µmol; $\phi = 0.0782 \pm 0.0031$.

1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene (475.9 mg, 1188

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(50) An epoxy adhesive not containing aromatic or other low-energy chromophores was used to cement quartz faces to Pyrex.

(51) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1965).

(52) W. G. Leighton and G. S. Forbes, *J. Amer. Chem. Soc.*, **52**, 3139 (1930).

μmol) added to ^{3}H photolysate (7.2 mg, 17.9 μmol): 8, 198.2 mg, 110–111.5°, 6.227 ± 0.055 μCi/mmol; 180 μmol recovered.

Run 2. 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene-^{3}H (76.8 mg, 191.7 μmol), activity 416.37 μCi/mmol in 39.0 ml of cyclohexane irradiated through monochromator (band width 22 nm) at 250 nm and 24°, 43.50 μEinsteins; analysis by liquid scintillation counting.

1,1-Diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane (494.1 mg, 1233 μmol) added to ^{3}H photolysate (69.1 mg, 172.5 μmol): 10, 205.6 mg, 139.5–141°, 1.069 ± 0.010 μCi/mmol; 3.527 μmol; $\phi = 0.0811 \pm 0.0032$.

1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene (498.3 mg, 1244 μmol) added to ^{3}H photolysate (7.7 mg, 19.2 μmol): 8, 157.1 mg, 110–111.5°, 6.297 ± 0.056 μCi/mmol; 191.0 μmol recovered.

Run 3. 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene-^{3}H (38.9 mg, 97.1 μmol), activity 416.37 μCi/mmol, and 1.988 g of benzophenone (10.92 mmol, 0.280 M) in 39.0 ml of cyclohexane irradiated through a monochromator (band width 22 nm) at 313 nm and 24°, 186.08 μEinsteins; analysis by liquid scintillation counting.

1,1-Diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane (299.5 g, 747.6 μmol) added to ^{3}H photolysate (35.0 mg, 87.4 μmol): 10, 154.6 mg, 139.5–141°, 0.434 ± 0.004 μCi/mmol; 0.866 μmol; $\phi = 0.0047 \pm 0.0002$.

1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene (668.9 mg, 1670 μmol) was added to ^{3}H photolysate (3.9 mg, 9.7 μmol): 8, 398.9 mg, 110–111.5°, 2.544 ± 0.024 μCi/mmol; 102.7 μmol recovered.

Run 4. 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene-^{3}H (59.8 mg, 149.3 μmol), activity 416.37 μCi/mol, and 2.125 g of propiophenone (15.86 mmol, 0.407 M) in 39.0 ml of cyclohexane irradiated through a monochromator (band width 22 nm) at 313 nm and 24°, 307.6 μEinsteins; analysis by liquid scintillation counting.

1,1-Diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane (432.2 mg, 1079 μmol) added to ^{3}H photolysate (53.8 mg, 134.4 μmol): 10, 139.7 mg, 139.5–141°, 1.098 ± 0.011 μCi/mmol; 3.169 μmol); $\phi = 0.0103 \pm 0.0004$.

1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene (488.7 mg, 1120 μmol) was added to ^{3}H photolysate (6.0 mg, 14.9 μmol): 8, 254.1 mg, 110–111.5°, 5.077 ± 0.044 μCi/mmol; 150.6 μmol recovered.

Run 5. 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene-^{3}H (38.3 mg, 95.6 μmol), activity 416.37 μCi/mmol, and 32.536 g of chlorobenzene (289.06 mmol, 7.410 M) in cyclohexane to bring the volume to 39.0 ml irradiated through monochromator (band width 22 nm) at 263 nm and 24.0°, 80.1 μEinsteins; analysis by liquid scintillation counting.

1,1-Diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane (313.2 mg, 781.8 μmol) was added to ^{3}H photolysate (34.5 mg, 86.0 μmol): 12, 117.9 mg, 139.5–141°, 0.600 ± 0.006 μCi/mmol; 1.254 μmol; $\phi = 0.0096 \pm 0.0004$.

1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene (403.6 mg, 1007.5 μmol) was added to ^{3}H photolysate (3.8 mg, 9.6 μmol): 8, 238.8 mg, 110–111.5°, 3.919 ± 0.035 μCi/mmol; 95.8 μmol recovered.

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