

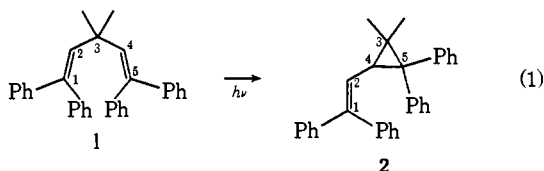
$\sigma + \pi$ Rearrangements of Di- π -methane Systems. Central Substitution and Di- π -methane Reactivity. Mechanistic and Exploratory Organic Photochemistry. LXXVI¹

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Abstract: The photochemistry of 1,1,5,5-tetraphenyl-1,4-pentadiene was investigated in order to ascertain the role of central alkyl substitution on the di- π -methane rearrangement. The photochemistry was compared with that of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene studied previously. A requirement of central substitution for facile di- π -methane reactivity was demonstrated. In the present instance, the product expected of the di- π -methane rearrangement of 1,1,5,5-tetraphenyl-1,4-pentadiene was actually observed as one of two products. However, by isotopic labeling it was demonstrated that this product derived instead from a $\sigma + \pi$ process in which the central C-H bond added across a double bond. A second product was 2,2,5,5-tetraphenylbicyclo[2.1.0]pentane. This housane arose by a unique diversion of a diradical species of the $\sigma + \pi$ route and not by direct 2 + 2 cycloaddition. Both reactions were shown to be singlet processes. The reactivity of the noncentrally substituted system was shown to be low both in terms of quantum efficiency and also on the basis of the rate of excited state rearrangement.

The di- π -methane rearrangement most typically involves the conversion of a divinylmethane such as 1 into a vinylcyclopropane product as 2 by a mechanism beginning with vinyl-vinyl bridging.² Operationally, the reaction can be defined by the skeletal change in eq 1. The present research was predicated on a pe-



culiar absence in the literature of di- π -methane examples lacking central substitution (*i.e.* having no substituents on the methane carbon three).³ For this study 1,1,5,5-tetraphenyl-1,4-pentadiene⁴ (3) was selected.

Exploratory Photochemical Studies and Product Elucidation. Irradiation of pentadiene 3 in *tert*-butyl alcohol with a 450-W medium-pressure lamp, using a glass short cut-off filter absorbing below 260 nm,⁵ gave two products in what appeared qualitatively to be a relatively inefficient process. Typically, from 1.00 g of pentadiene 3, irradiation for 24 hr afforded 120 mg of photoproduct 4, mp 101–102°, 110 mg of photoproduct 5, mp 180–181°, together with 710 mg of recovered reactant. The product mixture was nicely separated by reverse phase partition chromatography on polystyrene beads as previously described.²

(1) For paper LXXV of the series note: H. E. Zimmerman, R. J. Boettcher, and W. Braig, *J. Amer. Chem. Soc.*, **95**, 2155 (1973).

(2) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969).

(3) Gas phase photochemistry does provide examples of vinylcyclopropanes being formed from noncentrally substituted pentadienes with mercury sensitization. For example note: J. Meinwald and G. W. Smith, *J. Amer. Chem. Soc.*, **89**, 4923 (1967); R. Srinivasan and K. H. Carrough, *ibid.*, **89**, 4932 (1967).

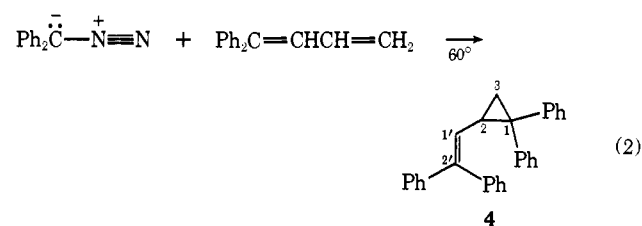
(4) G. Wittig and B. Obermann, *Ber.*, **67**, 2053 (1934); **68**, 2214 (1935).

(5) The Corex filter used was checked and found to cut off below 260 nm. We have been informed (private communication) by Professor H. Morrison that presently available Corex no longer is opaque at this wavelength.

One obvious candidate for a product structure was 1,1-diphenyl-2-(2',2'-diphenylvinyl)cyclopropane (4), the compound expected from a di- π -methane rearrangement of pentadiene 3. Of the two products, 4 had an nmr consisting of a 1H vinyl doublet, a 20H aromatic peak, and two complex aliphatic multiplets corresponding to an ABC pattern and ascribable to a -CHCH₂- moiety where the two methylene hydrogens are non-equivalent.

On-line computer simulation⁶ of the four proton portion of the molecule, namely =CH-CH-CHH', led to chemical shifts of τ_2 7.64, τ_{3c} 8.50 (where c refers to the cis configuration relative to H-2), τ_{3t} 8.46, and $\tau_{1'}$ 4.84 as well as coupling constants of $J_{23c} = 9.0$ cps, $J_{23t} = 5.5$ cps, $J_{33} = -6.0$ cps, and $J_{21'} = 10.0$ cps. With these constants an exact duplication of the experimental spectrum resulted, and the constants are reasonable on the basis of the structure of 1,1-diphenyl-2-(2',2'-diphenylvinyl)cyclopropane (4).

Final confirmation of this structural assignment was obtained from synthesis of vinylcyclopropane 4 utilizing the reaction of diphenyldiazomethane with 1,1-diphenyl-1,3-butadiene as shown in eq 2.

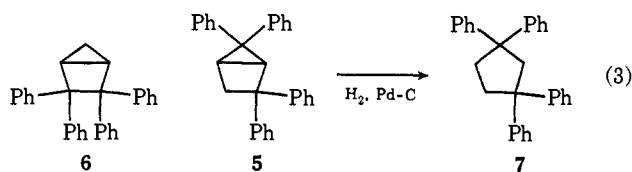


The second photoproduct (*i.e.*, 5) had an nmr spectrum which revealed only 20 aromatic hydrogens together with four aliphatic protons, indicating the absence of unsaturation. Similarly, the ultraviolet spectrum indicated the presence of four isolated phenyl groups. Initially, the simple 2 + 2 cycloaddition product 6 seemed possible. However, with the philosophy

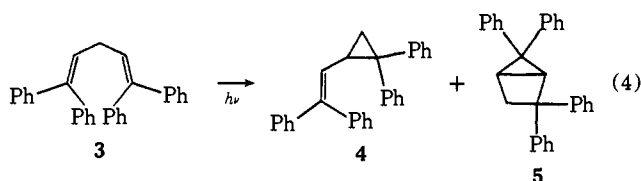
(6) (a) D. Juers, R. Boettcher, V. J. Hull, and H. E. Zimmerman, Digital Equipment Users Society program No. 8-194; (b) D. Juers, Ph.D. Thesis, University of Wisconsin, 1971.

that structural assignments made with nmr evidence alone are risky, and with clues provided by irradiation runs on labeled material (note below), we proceeded to obtain degradative structure proof.

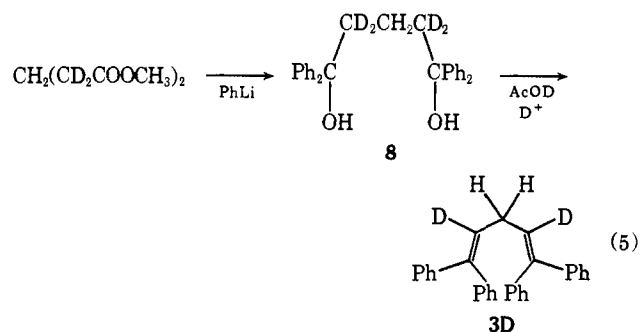
Catalytic hydrogenolysis using palladium on carbon afforded 1,1,3,3-tetraphenylcyclopentane⁷ (7) which was independently synthesized. This approach confirmed the presence of the five-membered ring of a housane but revealed a placement of phenyl groups 1,3 to one another and not 1,2 as in a simple 2 + 2 adduct. Rather, the evidence supported 2,2,5,5-tetraphenylbicyclo[2.1.0]pentane as the structure of the 180–181° photoproduct 5. The degradation is shown in eq 3.



Thus the photochemistry of 1,1,5,5-tetraphenyl-1,4-pentadiene (3) can be described as in eq 4.



Determination of Structural Aspects of the Rearrangements by Labeling. Because of the unusual nature of the rearrangement affording housane 5 and also because the formation of vinylcyclopropane 4 seemed suspiciously inefficient (note also the quantitative studies below), it was decided to study the photochemistry of labeled tetraphenyldiene 3. Rather than label the central carbon with deuterium, an easier approach proved to utilize deuterium labeling of the vinyl. A simple approach began with the reaction of phenyllithium and α -deuterated methyl glutarate⁸ followed by acid-catalyzed dehydration of the resulting labeled 1,1,5,5-tetraphenyl-1,5-pentenediol (8) using the method of



Wittig⁴ except with substitution of *O*-deuterioacetic acid (note eq 5). The method afforded 73% deuterated material which proved satisfactory for nmr analysis.

Irradiation of 2,4-dideuterio-1,1,5,5-tetraphenyl-1,4-pentadiene (3D) led to the two usual photoproducts, however, doubly deuterated. For a di- π -methane rearrangement, the original central methylene (*i.e.*, C-3)

(7) D. H. Richards and N. F. Scilly, *J. Chem. Soc. C*, 2661 (1969).
 (8) J. D. Lambert and R. G. Keske, *J. Org. Chem.*, 31, 3429 (1966).

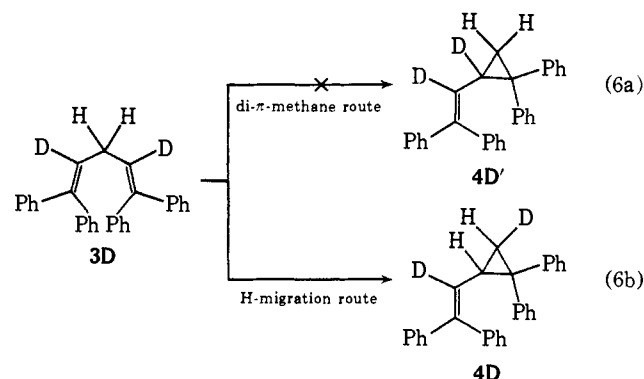
of pentadiene 3 would become the cyclopropane methylene of the vinylcyclopropane product (here 4D'). This proved not to be the case (note Table I). Rather,

Table I. Relative Nmr Peak Areas^a for 1,1-Diphenyl-2-(2',2'-diphenylvinyl)cyclopropane

	Cyclopropyl methylene	Cyclopropyl methine	Vinyl
Run 1	54	34	12
Run 2	50	36	13
Calcd for a di- π -methane mech	78	11	11
Calcd for a H-migration mech	50	39	11

^a Expressed as a percentage of the total area (excluding aromatics).

the nmr of the vinylcyclopropane product 4D revealed a much lower amount of hydrogen at the cyclopropyl-methylene. Comparison of the deuterium distribution anticipated on the basis of a hydrogen migration mechanism (note discussion below) with that actually observed proved in accord not only with the prediction for the methylene but also for the methine and vinyl hydrogen contents (note Table I again). Thus the gross molecular change is as pictured in eq 6b rather than 6a.



Consideration of the limits of detection indicated that any incursion of the di- π -methane route in eq 6a above 10% would have been observable.

In the case of the housane product 5D, the nmr of the product revealed an AB quartet signifying two coupled hydrogens (Table II). On Pd-C catalytic hydrogenation

Table II. Relative Nmr Peak Areas^a for 2,2,5,5-Tetraphenylbicyclo[2.1.0]pentane

	One-proton multiplet	Three-proton multiplet
Run 1	88	12
Run 2	89	11
Calcd for structure 5D	89	11

^a Expressed as a percentage of the total area (excluding aromatics).

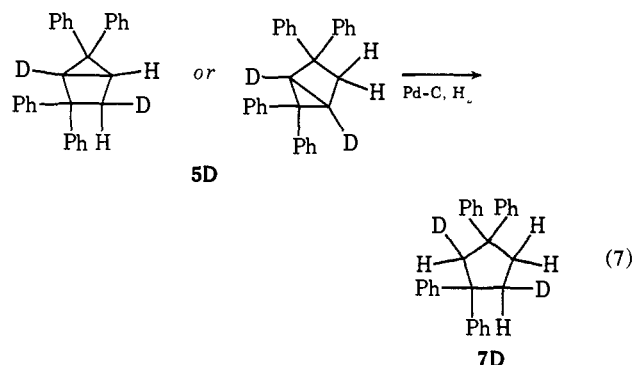
tion parallel to that described above for the undeuterated material, deuterated 1,1,3,3-tetraphenylcyclopentane (7D) was obtained. This product exhibited the two sharp singlets characteristic of undeuterated cyclopentane 7 but with the methylene and ethylene bridge areas being now in a 1:3 ratio (after correction

Table III. Singlet Excited State Rate Constants and Quantum Yields for Vinylcyclopropane Formation

Compd	ϕ_f	ϕ_r	k_f, sec^{-1}	k_{dt}, sec^{-1}	k_r, sec^{-1}	$k_d,^f \text{sec}^{-1}$	Ref
$\text{Ph}_2\text{C}=\text{CH}_2$	300×10^{-5}		2.6×10^8	8.7×10^{10}		8.7×10^7	10
Diene 1 ^{a,c}	7.6×10^{-5}	0.08	7.3×10^8	9.7×10^{12}	7.8×10^{11}	8.9×10^{12}	10
Diene 1 ^{a,d}	1.3×10^{-5}	0.08	7.3×10^8	5.6×10^{13}	4.5×10^{12}	5.1×10^{13}	This work
Diene 1 ^{a,e}	5.0×10^{-5}	0.08	7.3×10^8	1.5×10^{13}	1.2×10^{12}	1.4×10^{13}	This work
Diene 3 ^{b,c}	1.1×10^{-4}	0.0024	5.7×10^8	5.2×10^{12}	1.2×10^{10}	5.2×10^{12}	This work
Diene 3 ^{b,d}	1.8×10^{-5}	0.0024	5.7×10^8	3.1×10^{13}	7.4×10^{10}	3.1×10^{13}	This work
Diene 3 ^{b,e}	6.9×10^{-5}	0.0024	5.7×10^8	8.3×10^{12}	2.0×10^{10}	8.3×10^{12}	This work

^a Refers to 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene. ^b Refers to 1,1,5,5-tetraphenyl-1,4-pentadiene. ^c Hg lamp used for excitation, $\text{Ph}_2\text{C}=\text{CH}_2$ standard. ^d Xenon lamp, $\text{Ph}_2\text{C}=\text{CH}_2$ standard. ^e Xenon lamp, naphthalene standard ($\phi_f = 0.23$; I. B. Berlman, "Handbook of Fluorescent Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, p 104. Note also the similar values quoted by J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, N. Y., 1970, p 126). ^f k_d , the rate of radiationless decay, is defined by $k_d = k_{dt} - k_r - k_f$.

for 27% residual hydrogen) compared with the 1:2 ratio found for undeuterated cyclopentane 7. As a result, the cyclopentane product must have the deuterium distribution of 7D in eq 7 and photoproduct 5D



must have one of the two distributions shown in eq 7. Finally, recovered diene 3D showed no scrambling within experimental error.

Reaction Efficiencies and Multiplicity. Results. Confirming qualitative impression from the exploratory efforts, it was found that the reaction efficiency was indeed low. Thus the quantum yield of formation of vinylcyclopropane 4 in direct irradiation was determined as $\phi = 0.0024$. That for the housane product 5 was $\phi = 0.0020$.

Sensitization runs with acetophenone in *tert*-butyl alcohol were under conditions where the concentration of reactant was sufficiently high to allow efficient transfer of triplet excitation but low enough to preclude singlet sensitization.⁹ However, it was found that no product of triplet excitation resulted. Thus it can be concluded that both vinylcyclopropane 4 and housane 5 arise from the singlet excited state of pentadiene 3 and that the corresponding triplet is unreactive.

Excited State Reactivity and Rates. It was recognized that mere measurement of the reaction quantum yield really does not afford a reliable indication of inherent excited state reactivity. Rather, in comparing inherent reactivity of the presently investigated excited state with that of previous systems, one should have available the rates of excited state rearrangement.

Previously, we have described a simple approach for obtaining such rate constants¹⁰ and this method has been independently reported by Dalton and Turro.¹¹

(9) Note ref 2 for a discussion of the basis for selecting conditions.

(10) H. E. Zimmerman and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 3646 (1971).

(11) J. C. Dalton and N. J. Turro, *ibid.*, **93**, 3569 (1971).

The method uses the relation in eq 8, where k_r is the

$$k_r = k_f \phi_r / \phi_f \quad (8)$$

desired singlet reaction rate, k_f is the corresponding fluorescence rate, ϕ_f is the fluorescence quantum yield, and ϕ_r is the reaction quantum yield. The last three values are readily obtained experimentally.

Thus k_r was determined presently and compared with the values obtained for the corresponding centrally substituted tetraphenyl diene 1. For obtaining the necessary fluorescence quantum yields, a standard compound is required. Diphenylethylene was used in our earlier study and was again employed because of its similar spectral characteristics relative to the compound of interest. However, it seemed worthwhile to check the results using a more intensively studied reference compound and the results were repeated with a naphthalene standard.

One further quantity obtainable was k_{dt} , the total rate of singlet decay. Thus k_{dt} is defined by eq 9 which

$$\phi_f = k_f / k_{dt} \quad (9)$$

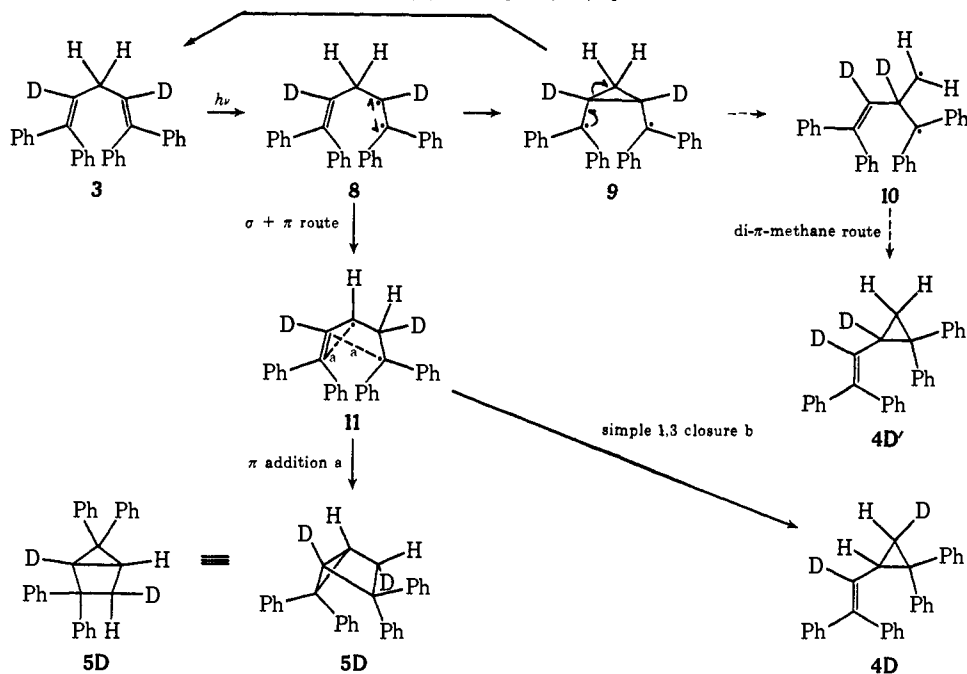
relates the fluorescence quantum yield and rate.

The results of the present study, along with the values obtained earlier, are collected in Table III. It is noted that there is modest scatter of the results obtained for each diene using different fluorescent quantum yield standards and conditions as shown. This variation derives partially from experimental difficulties resulting from weakness of the fluorescence emission and partially from use of different literature measurements as standards. However, with any one standard the variations are remarkably minor considering the orders of magnitude variation of the rate constants of interest, and in any case, for comparison of the relative rates of different compounds the method is most useful.¹²

Interpretative Discussion. Gross Mechanistic Aspects of the Rearrangements. The observation of 1,1-diphenyl-2-(2',2'-diphenylvinyl)cyclopropane (4) as one of the products of direct photolysis of the tetraphenyl diene 3 initially suggested that an ordinary di- π -methane rearrangement was occurring. The skeletal transformation certainly is characteristic of the di- π -methane reaction. However, the deuterium labeling studies cited above (*cf.* Results section) definitively exclude this mechanism. Rather, the location of the label in the vinylcyclopropane product 4 requires a hydrogen migration mechanism in which a hydrogen on

(12) Studies improving this method and employing single photon counting techniques are in progress.

Chart I. Reaction Pathways in the Direct Irradiation of 1,1,5,5-Tetraphenyl-1,4-pentadiene



the methane carbon migrates to the adjacent diphenylvinyl group. The unobserved di- π mechanism and the observed $\sigma + \pi$ hydrogen migration route are both depicted in Chart I.

The most remarkable aspect of the mechanisms is their close relationship. Thus, after the 1,2-sigmatropic hydrogen migration to give biradical species 11, simple three-ring closure gives vinylcyclopropane product 4 while addition of the odd electron centers across the remaining π bond gives housane 5. Interesting, a third mode of closure of species 11 would give 3,3,4,4-tetraphenylcyclopentene, but this product was not detected.

Multiplicity and Quantitative Aspects. Interpretative Discussion. The occurrence of the vinylcyclopropane and housane forming reactions only on direct irradiation and the total lack of reactivity under sensitized conditions reveal that the observed photochemistry derives from the singlet excited state of tetraphenyl-1,4-pentadiene 3 and also demonstrate that the triplet excited state merely dissipates energy by intersystem crossing to the ground state. This behavior has analogy in our previous studies where the presence of a nonconstrained double bond was found to lead to rapid energy degradation in what was termed a "free rotor effect."^{2,10,13,14} Presently the free rotor is one of the diphenylvinyl groups.

Similarly, the considerable reactivity of the first singlet excited state has analogy in the photochemistry of the previously studied di- π -methane systems,¹⁵ although presently the reactions occurring actually differ structurally. The singlet reactivity correlates well with the idea that first singlet excited states often find very facile routes to product ground states as a consequence of the interaction of two electrons with opposite spins to gradually generate one additional covalent bond as ground-state product is produced from the excited

singlet. This is especially true where the reaction is concerted as has previously been noted.¹⁶ In this connection, comment is needed that writing the reaction mechanism *via* the structures (or species) in Chart I does not connote necessary lack of concertedness. Such structures are conveniences which allow the organic chemist to describe molecular change during a reaction, and these species may correspond only to points along a potential energy surface leading to product. Nevertheless, focusing attention on any one species does provide some description of the reacting molecule and therefore does facilitate prediction of molecular behavior. Presently, sufficient evidence is not available to define degree of concertedness.

Turning now to the matter of reaction efficiency, we note that the observed quantum yields of $\phi = 0.0024$ and $\phi = 0.0020$ for the $\sigma + \pi$ reaction and the housane formation are low when one contrasts these with the $\phi = 0.08$ found for the di- π -methane rearrangement of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (1). The other di- π -methane systems have comparably high quantum yields. Thus the $\sigma + \pi$ reaction is indeed relatively inefficient.

However, as has often been noted by us previously^{10,17} and as pointed out above, reliance on quantum yield as a measure of inherent reactivity is imperfect, since quantum yields do not necessarily correlate with excited state reactivity. Specifically, the quantum yields are given by the ratio of the desired excited state reaction rates divided by the total rate of excited state decay, and this excited state decay will not be identical, in general, for two excited states being compared.

With this philosophy in mind, the singlet excited state rate constants obtained and delineated in Table I are of particular interest. Of primary interest is the unimolecular rate of $\sigma + \pi$ rearrangement of tetra-

(13) H. E. Zimmerman and G. E. Samuelson, *J. Amer. Chem. Soc.*, **91**, 5307 (1969).

(14) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6259 (1970).

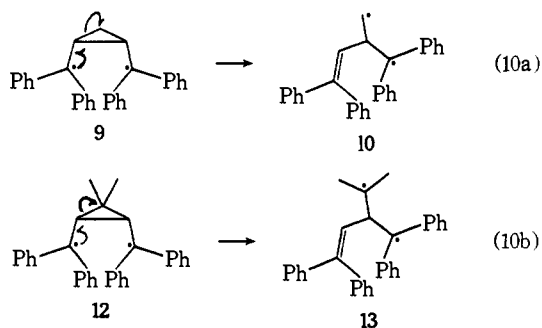
(15) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6267 (1970).

(16) (a) H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, **94**, 2647, 7806 (1972). (b) Note also the discussion by J. Michl, *Mol. Photochem.*, **4**, 243 (1972).

(17) H. E. Zimmerman and K. G. Hancock, *J. Amer. Chem. Soc.*, **90**, 3749 (1968).

phenyl diene **3** to give vinylcyclopropane **4**. This value,¹⁸ $k_r = 4.7 \times 10^{10} \text{ sec}^{-1}$, is very rapid; yet compared to the rate constant for the di- π -methane rearrangement of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**1**), $k_r = 2.9 \times 10^{12} \text{ sec}^{-1}$, the $\sigma + \pi$ rate is low.

This then confirms the impression given by the quantum yields that the $\sigma + \pi$ reaction is a relatively slow one compared with the di- π -methane rearrangement. A further consequence is evident. If in the photochemistry of tetraphenyl diene **3** there were any rearrangement by the di- π -methane route, the singlet excited state rate constant must be less than $4.7 \times 10^9 \text{ sec}^{-1}$ for the process to go unobserved (*vide supra*). Hence any di- π -methane rearrangement of 1,1,5,5-tetraphenyl-1,4-pentadiene (**3**) is at least *ca.* 600-fold slower than for the centrally dimethyl-substituted analog **1**. This is reasonably understood in terms of the mechanism which would have to be followed by the excited state of the tetraphenyl diene **3**; thus the ring-opening step to give species **10** affords odd electron density on a primary carbon, contrasting with the centrally substituted case where a tertiary center acquires odd electron density (note eq 10a and 10b).



It is seen that competition for the reacting species by the housane route is not a factor altering the substance of the discussion, since the unimolecular rate for the formation of housane **5** is comparable to that for vinylcyclopropane formation.

One further fascinating point is the exceedingly rapid rate of radiationless decay observed (note Table I). Thus the total rate of singlet decay, k_{dt} , may be dissected into its components. As can be seen from the table, the major component is k_d , the rate of radiationless decay to ground state. The value of $2 \times 10^{13} \text{ sec}^{-1}$ found for tetraphenyl diene **3** is very close to the rate of a molecular (*e.g.*, C-C) vibration. The value is quite similar to that found presently (note Table I) and earlier¹⁰ for 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**1**).

One intriguing possibility is that the decay derives from the bridging process which ordinarily leads to di- π -methane rearrangement; note steps **8** \rightarrow **9** and **9** \rightarrow **3** in Chart I. Thus bridging (**8** \rightarrow **9**) could be very rapid, and the fission of the central bond of a 1,4-biradical species as **9** is commonplace and presently leads to reactant **3**. Supporting this suggestion is the close similarity in rates of decay for the tetraphenyl diene **3** and 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**1**). The three-ring closure is common to both di- π -methane molecules. However, the tetraphenyl diene **3** has very unfavorable energetics for the ring opening required for

the di- π -methane route (note eq 10a) compared with the centrally substituted diene **1** (note eq 10b). Thus it is not surprising that the di- π -methane rearrangement rates can differ by at least 600-fold (*vide supra*) and yet the decay rates can be so similar.

A general and important point needs some commentary. This is whether it is worrisome to find decay and reaction rates of excited states which approach or exceed the rate of a typical molecular vibration. In instances where the excited species is generated on a hypersurface which leads downward in energy toward product or toward a species reverting to reactant (*i.e.*, corresponding to reaction or radiationless decay, respectively), the rate actually being measured is the molecular distortion, ΔR , sufficient to preclude further fluorescence emission. This is a consequence of using eq 8 and 9 to obtain k_r and k_{dt} ; these are used together with k_t to get k_d (note above). However, ΔR then may be a relatively small molecular change and need not require molecular change corresponding to a full vibration.

General Conclusions

The most striking aspect of the present study is the observation that in absence of central substitution, the acyclic di- π -methane rearrangement occurs very slowly if at all. Additionally, the singlet photochemistry which then occurs involves instead $\sigma + \pi$ processes.

However, the conclusion should not be extended to systems containing one double bond and one aryl group as is evidenced by the work of Griffin¹⁹ and also the work of Hixson.²⁰ In both cases, aryl groups were demonstrated to migrate to the terminal position of a styryl chromophore despite the methane carbon bearing two hydrogens. It seems likely that the π - π bridged species in this case has excess driving force for three-ring opening, in contrast with the di-vinylmethane systems, due to regeneration of the aromatic ring.

The hydrogen migration found in the present work does have precedent in the Griffin study where hydrogen migration was also observed; however, in this instance no di- π -methane rearrangement was possible.

Another point needing comment concerns the literature examples of simple aliphatic divinylmethanes which give vinylcyclopropane products in the gas phase and with mercury sensitization.³ Although most of these could be formulated as di- π -methane rearrangements, they are equally well envisaged with present evidence available as C-H $\sigma + \pi$ reactions.

Hence, it is seen that there is a delicate balance in the competition between di- π -methane and $\sigma + \pi$ rearrangement routes and that these can be assessed on a quantitative basis despite the exceedingly rapid rates of the excited singlet rearrangements.

Experimental Section²¹

1,1,5,5-Tetraphenyl-1,4-pentadiene. This compound was synthesized as described by Wittig,⁴ mp 77–78° (lit. 76–77°); the spectral data were: nmr (CCl₄) τ 7.0 (t, $J = 8$ cps, 2 H, CH₂), 3.87 (t, $J = 8$ cps, 2 H, vinyl), 2.72 (s, 20 H, arom); uv max (MeOH) 263 nm (ϵ 25,500).

Photolysis of 1,1,5,5-Tetraphenyl-1,4-pentadiene in *tert*-Butyl

(19) G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Peterson, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965).

(20) S. Hixson, *J. Amer. Chem. Soc.*, **94**, 2507 (1972).

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

(18) The values used are the averages of the xenon lamp runs in Table I, these being selected as the most reliable.

Alcohol. A solution of 1.00 g of 1,1,5,5-tetraphenyl-1,4-pentadiene in 1000 ml of *tert*-butyl alcohol was photolyzed for 24 hr using a 450-W medium-pressure Hanovia mercury lamp filtered through a 1-mm Corex⁵ glass filter. Removal of the solvent gave 1.03 g of a yellow crystalline mass. The mixture was then chromatographed using a 3 × 204 cm column by reverse phase methanol-cyclohexane liquid-liquid partition chromatography on polystyrene beads as described previously.² The eluent was scanned at 260 nm and 40-ml fractions were collected. Fractions 77-93 contained 33.8 mg of an unknown compound; fractions 100-112, 87.8 mg of 1,1-diphenyl-2-(2',2'-diphenylvinyl)cyclopropane; fractions 113-116, 30.1 mg of overlap; fractions 117-126, 112.7 mg of 2,2,5,5-tetraphenylbicyclo[2.1.0]pentane; fractions 127-164, 714.4 mg of the starting tetraphenyldiene. The mass balance of the three recovered hydrocarbons was 945 mg (95%) and the conversion to photo-products was 231 mg (23%).

Fractions 100-112 were recrystallized from ethanol and then sublimed at 100° and 1 mm to give pure 1,1-diphenyl-2-(2',2'-diphenylvinyl)cyclopropane: mp 101-102°; nmr (CCl₄) τ 8.50 (m, $J(\text{gem}) = -6$ cps, $J(\text{cis}) = 9$ cps, 1 H, cyclopropyl CH₂ hydrogen cis to H-2), 8.46 (m, $J(\text{gem}) = -6$ cps, $J(\text{trans}) = 5.5$ cps, 1 H, cyclopropyl CH₂ trans to H-2), 7.64 (m, $J(\text{cis}) = 9$ cps, $J(\text{trans}) = 5.5$ cps, $J(\text{vinyl}) = 10$ cps, 1 H, cyclopropyl methine), 4.84 (d, $J = 10$ cps, 1 H, vinyl), 3.0-2.7 (m, 20 H, arom). The chemical shifts and coupling constants for this compound were determined by on-line graphic computer simulation.⁶ Other spectral properties were: ir (CCl₄) 3.25, 3.29, 6.27, 6.70, 6.92, 8.85, 9.71, 14.3 μ ; uv max (MeOH) 268 nm (ϵ 19,200).

Anal. Calcd for C₂₀H₂₄: C, 93.51; H, 6.49. Found: C, 93.41; H, 6.53.

Fractions 117-126 were recrystallized twice from ethanol to give the pure 2,2,5,5-tetraphenylbicyclo[2.1.0]pentane: mp 180-181°; nmr (CCl₄) τ 7.50 (m, 3 H), 6.97 (m, 1 H), 3.4-2.5 (m, 20 H, arom); ir (CCl₄) 3.25, 3.30, 6.27, 6.71, 6.95, 9.75, 14.4 μ ; uv max (hexane) 273 nm (ϵ 756), 263 (1080).

Anal. Calcd for C₂₀H₂₄: C, 93.51; H, 6.49. Found: C, 93.44; H, 6.62.

1,1-Diphenyl-2-(2',2'-diphenylvinyl)cyclopropane. A mixture of 1.31 g (6.75 mmol) of freshly prepared diphenyldiazomethane²² and 2.65 g (12.9 mmol) of 1,1-diphenyl-1,3-butadiene^{23,24} was heated at 60° for 6 days and then heated to 120° for 2 hr. After cooling, the mixture was taken up in 10 ml of hexane and the benzophenone azine that crystallized was filtered. The filtrate was concentrated *in vacuo* to give 2.81 g of a pale yellow oil which was chromatographed on a 4.5 × 76 cm silica gel column (Matheson Coleman and Bell, Grade 62, 60-200 mesh) using 0.25% ether in hexane as the eluent. The 2500-4000-ml fraction contained 1.01 g (40% based on diphenyldiazomethane) of the desired 1,1-diphenyl-2-(2',2'-diphenylvinyl)cyclopropane, mp 98-99°. One crystallization from ethanol gave the pure vinylcyclopropane, mp 101-102°; identical in melting point and spectral properties as from the photolysis.

Catalytic Reduction of 2,2,5,5-Tetraphenylbicyclo[2.1.0]pentane. A 34.1-mg sample of 2,2,5,5-tetraphenylbicyclo[2.1.0]pentane in 10 ml of ethanol was hydrogenated at atmospheric pressure using 58 mg of 10% Pd-C. Since the expected uptake of hydrogen was too small to measure reliably, the reaction was run for 15 hr. Filtration of the catalyst and removal of the solvent gave 26 mg of a white crystalline compound. One recrystallization from ethanol gave 21 mg of pure 1,1,3,3-tetraphenylcyclopentane; mp 133-134° (lit.⁷ 133-134°); nmr (CCl₄) τ 7.57 (s, 4 H, C-4 and C-5 CH₂), 6.20 (s, 2 H, C-2 CH₂), 2.95 (s, 20 H, arom). This material was identical with the independently synthesized compound.⁷

Quantum Yields for the Rearrangement of 1,1,5,5-Tetraphenyl-1,4-pentadiene. All quantum yield irradiations were performed on the Black Box apparatus described previously.²⁵ Light output was monitored by ferrioxalate actinometry²⁶ and the light absorbed in the reaction cell was determined by the splitting ratio technique described.²⁵ The bandpass was controlled by one of the following filter solutions: filter A, 1.0 M NiSO₄·6H₂O in 5% H₂SO₄, 1.0 M CoSO₄·7H₂O in 5% H₂SO₄, 2 × 10⁻⁴ M BiCl₃ in 10% HCl; transmission, 0% at 245 nm, 30% at 283 nm, 0% at 305 nm; filter B, 1.0

M NiSO₄·6H₂O in 5% H₂SO₄, 1.0 M CoSO₄·7H₂O in 5% H₂SO₄, 0.015 M SnCl₂·2H₂O in 10% HCl; transmission, 0% at 302 nm, 43% at 322 nm, 0% at 355 nm.

The quantum yields for product formation were determined by vpc analysis using a 0.25 in. × 6 ft 5% QF-1 on Varaport-30 column at 190° and 20 ml/min flow rate. Tetraphenylethylene was used as an internal standard. Retention times were: 1,1-diphenyl-2-(2',2'-diphenylvinyl)cyclopropane, 32 min; 2,2,5,5-tetraphenylbicyclo[2.1.0]pentane, 38 min; 1,1,5,5-tetraphenyl-1,4-pentadiene, 47 min. The flame ionization detector of the Varian Aerograph Model 2100 gas chromatograph was calibrated for the relative response of the compounds in the photolysate and the standard. The estimated precision of the quantum yields is ±10% based on the total error in the actinometry and the analysis.

Summary of Quantum Yield Results. Data are listed as follows: filter, solvent and volume, starting 1,1,5,5-tetraphenyl-1,4-pentadiene (mmol), light absorbed, 1,1-diphenyl-2-(2',2'-diphenylvinyl)cyclopropane formed (mmol), quantum yield, 2,2,5,5-tetraphenylbicyclo[2.1.0]pentane formed (mmol), quantum yield, and per cent conversion.

Run I-1. Filter A, 750 ml of *tert*-butyl alcohol, starting diene (0.535 mmol), 9.84 mEinstein, vinylcyclopropane (0.022 mmol), $\phi = 0.0022$, bicyclopentane (0.019 mmol), $\phi = 0.0019$, conversion 7.7%.

Run I-2. Filter A, 750 ml of *tert*-butyl alcohol, starting diene (0.537 mmol), 5.18 mEinstein, vinylcyclopropane (0.014 mmol), $\phi = 0.0026$, bicyclopentane (0.012 mmol), $\phi = 0.0023$, conversion 4.8%.

Run I-3. Filter A, 750 ml of *tert*-butyl alcohol, starting diene (0.538 mmol), 2.26 mEinstein, vinylcyclopropane (0.0055 mmol), $\phi = 0.0024$, bicyclopentane (0.0043 mmol), $\phi = 0.0019$, conversion 1.8%.

Run I-4. Filter B, 750 ml of *tert*-butyl alcohol, starting diene (1.075 mmol), acetophenone (0.234 mol), 6.0 mEinstein, vinylcyclopropane and bicyclopentane (none detectable), $\phi \leq 0.00002$.

Dimethyl $\alpha,\alpha,\alpha',\alpha'$ -Tetradeterioglutarate. The method of Lambert and Keske²⁷ was used. A solution of 3.20 g (0.02 mol) of dimethyl glutarate and 200 mg of sodium methoxide in 5.0 ml of methanol-*O*-*d*²⁸ was refluxed for 0.5 hr. The reaction was then poured into 100 ml of water, the mixture extracted with 4 × 25 ml of ether, and the ether was dried over MgSO₄, filtered and concentrated *in vacuo* to give 2.89 g of the partially deuterated ester. After five such exchanges, the yield of 95% (by nmr integration) deuterated ester was 1.60 g (50%).

2,2,4,4-Tetradeterio-1,1,5,5-tetraphenyl-1,4-pentanediol. A solution of 1.9 g (11.3 mmol) of dimethyl $\alpha,\alpha,\alpha',\alpha'$ -tetradeterioglutarate in 30 ml of ether was added over 0.5 hr to a solution of 55.0 mmol of phenyllithium in 50 ml of ether. After refluxing another 0.5 hr the reaction mixture was poured into ice water, ether layer separated and dried over MgSO₄ and the solvent removed *in vacuo* to give 4.35 g of pale yellow crystals. One crystallization from benzene gave 3.23 g (70%) of the pure diol, mp 115-116°. Nmr integration gave the deuterium content as 95% in the 2 and 4 positions.

2,4-Dideuterio-1,1,5,5-tetraphenyl-1,4-pentadiene. A solution of 1.50 g (3.62 mmol) of 2,2,4,4-tetradeterio-1,1,5,5-tetraphenyl-1,5-pentanediol in 7.5 ml of acetic acid-*d*²⁹ was refluxed for 0.5 hr. On cooling an oil separated and crystallized on standing. Filtration gave 1.23 g (89%) of the diene. This material was then chromatographed on a 4 × 30 cm silica gel column with the top 10 cm containing decolorizing charcoal. Elution with 2% ether in hexane gave the diene in the 200-1000-ml fraction. Ethanol recrystallization gave 823 mg of the pure diene, mp 76-77°. Nmr analysis indicated a deuterium content of 71% in the vinyl positions.

Photolysis of 2,4-Dideuterio-1,1,5,5-tetraphenyl-1,4-pentadiene. A solution of 406 mg of the deuterated diene in 500 ml of *tert*-butyl alcohol was photolyzed for 12 hr using a 450-W medium-pressure Hanovia mercury lamp filtered through 1-mm Corex glass.⁵ The reaction mixture was chromatographed on the methanol-cyclohexane liquid-liquid system used previously (*vide supra*). Fractions 101-117 contained 59.2 mg of deuterated 1,1-diphenyl-2-(2',2'-diphenylvinyl)cyclopropane which was recrystallized from ethanol to give 28.6 mg of the pure compound, mp 100-101°. Fractions 118-130 contained 64.3 mg of deuterated 2,2,5,5-tetraphenyl-

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[2.1.0]pentane which was recrystallized from ethanol to give 31.0 mg of the pure compound, mp 179–180°. Fractions 142–166 contained 172 mg of starting diene whose nmr spectrum showed no deuterium scrambling within experimental error.

The nmr (CCl_4) of the deuterated vinylcyclopropane consisted of τ 8.50 (m, cyclopropyl CH_2 , rel area 45), 7.64 (m, cyclopropyl CH, rel area 28), 4.84 (d, $J = 10$ cps, vinyl, rel area 9.4). The nmr (CCl_4) of the deuterated bicyclo[2.1.0]pentane consisted of τ 7.82 (d, $J = 12$ cps, rel area 70), 7.40 (d, $J = 12$ cps, rel area 66), 6.98 (s, rel area 18).

A second identical run gave the following results: vinylcyclopropane, nmr (CCl_4) τ 8.50 (m, cyclopropyl CH_2 , rel area 40), 7.64 (m, cyclopropyl CH, rel area 26), 4.84 (d, $J = 10$ cps, vinyl, rel area 10); bicyclo[2.1.0]pentane, nmr (CCl_4) τ 7.82 (d, $J = 12$ cps, rel area 50), 7.40 (d, $J = 12$ cps, rel area 45), 6.98 (s, rel area 12).

Catalytic Reduction of Deuterio-2,2,5,5-tetraphenylbicyclo[2.1.0]pentane. A sample of deuterio-2,2,5,5-tetraphenylbicyclo[2.1.0]pentane obtained from photolysis of deuterated 1,1,5,5-tetraphenyl-1,4-pentadiene was catalytically reduced with 10% palladium on charcoal as described above. The nmr (CCl_4) indicated τ 7.57 (s, C-4 and C-5 CH_2 , rel area 23) and 6.20 (s, C-2 CH_2 , rel area 8.5).

Determination of the Fluorescence Quantum Yield of 1,1,5,5-Tetraphenyl-1,4-pentadiene and 1,1,5,5-Tetraphenyl-3,3-dimethyl-1,4-pentadiene. An Aminco-Keirs spectrofluorimeter was used to obtain the fluorescence quantum yield for the dienes by three different procedures.

This procedure was used previously by Zimmerman and Baum¹⁰ and involves measuring the fluorescence intensity relative to di-

phenylethylene ($\phi_f = 0.003^{30a}$) standard using a mercury lamp for excitation. Solutions were of equal optical density (5.0) at 254 nm, the wavelength of excitation.

Again diphenylethylene was used as a standard but in this case a xenon lamp was used for excitation. This obviates problems resulting from scattering of the mercury 310-nm line which could alter the intensities measured. Solutions of equal optical density (1.85) at the 254-nm wavelength of excitation were again used.

Alternatively, naphthalene ($\phi_f = 0.23^{30}$) was used as a standard for the fluorescence intensities again using the xenon lamp for excitation. Solutions of equal optical density (1.85) at the 254-nm wavelength of excitation were again used.

The results of these methods are compiled in Table III.

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Kinetic Application of Electron Paramagnetic Resonance Spectroscopy. IX. Preparation and Properties of Di-*tert*-butyliminoxy¹

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Abstract: Di-*tert*-butyl ketoxime has been prepared by a new and simple procedure. It can be oxidized by a variety of oxidizing agents to a moderately stable free radical, di-*tert*-butyliminoxy (**1**), a blue liquid, fp -21° . Some of the physical and chemical properties of **1** have been determined. It dimerizes slowly and irreversibly at room temperature, $2k_t = 2.1 \times 10^{-5} M^{-1} \text{sec}^{-1}$ in benzene at 24° . Di-*tert*-butylnitrimine is formed by reaction of **1** with nitric oxide. Hydrogen is abstracted by **1** from a variety of organic materials including phenols, triethylamine, triethyl phosphite, hydrazine, hydrazobenzene, 1,4-cyclohexadiene, toluene, ethylbenzene, cumene, and hydroxylamines. Kinetic studies have been made on some of these reactions.

Iminoxy^{2,3} radicals, $\text{RR}'\text{C}=\text{NO}\cdot$, derived from the corresponding oximes $\text{RR}'\text{C}=\text{NOH}$ by one-electron oxidation, have received considerable attention since their initial observation by Thomas⁴ in 1964. These radicals have, so far, been studied only by epr techniques since most of them dimerize or disproportionate rapidly.² A large body of information exists con-

cerning the epr spectra of these radicals,⁸⁻¹⁹ though to date none has been isolated and characterized in the pure state.

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