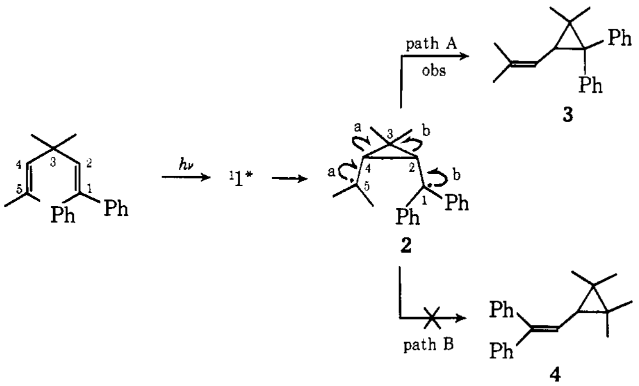
Electron Delocalization as a Controlling Factor in the Di-π-methane Rearrangement. Exploratory and Mechanistic Organic Photochemistry. LXII[1]

Howard E. Zimmerman* and Anthony A. Baum

Contribution from the Department of Chemistry, the University of Wisconsin, Madison, Wisconsin 53706. *Received September 1, 1970*

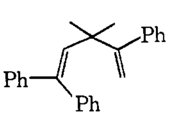
Abstract: The photochemistry of 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene was investigated. This triphenyldiene was found to rearrange on direct irradiation to give 1-α-styryl-2,2-diphenyl-3,3-dimethylcyclopropane as the major product. The alternative di-π-methane rearrangement product, 1-(2,2-diphenylvinyl)-1-phenyl-2,2-dimethylcyclopropane, was not produced. The rearrangement was shown to involve reaction of the singlet excited state of the diene and the corresponding triplet was demonstrated to be unreactive. The quantum efficiency of the singlet di-π-methane process was found to be 0.008. This is considerably less efficient than the previously studied di-π-methane rearrangement of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (ϕ = 0.080). This difference in efficiency was shown to derive from a two order of magnitude lower rate of excited state rearrangement for the diene presently studied compared with the tetraphenyldiene, the rates being 11×10^9 sec^{-1} and 8×10^{11} sec^{-1}, respectively. The rates of excited-state decay for 1,1-diphenylethylene, the triphenyldiene, and the tetraphenyldiene increased in this order but the variation with structure was relatively small. Both the directionality of the rearrangement of the triphenyldiene and its decreased rate of excited state rearrangement are discussed in terms of control by electron delocalization during reaction.

In our previous papers[2-4] we noted that a large number of photochemical rearrangements were structurally similar and could be understood using a mechanism whose first step was bridging between two π moieties; we termed this the di-π-methane rearrangement.[5] A particularly intriguing example was the rearrangement of 1,1-diphenyl-3,3,5,5-tetramethyl-1,4-hexadiene. Here only vinylcyclopropane **3** was formed, although in principle product **4** might have been anticipated also. It was suggested that the reaction directionality giving preference to path A derived from the higher odd electron density at C-5 relative to that at C-1 in species **2**.

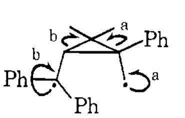


Although this rationale seemed to accord with observation, another factor which seemed possibly important in controlling the directionality was the different energies of the two excited π systems, dimethylvinyl *vs.* diphenylvinyl. One might have interpreted the reaction selectivity as signifying that the π system having the lower singlet excitation energy tends to be the one lost in the reaction. Especially if one were to simplify the mechanism of the di-π-methane rearrangement and envision one σ bond (*i.e.*, bond 3–4 in **1**) as adding across an electronically excited π bond (*i.e.*, 1–2 in **1**), it would be reasonable to expect the more readily excited π bond to be the one participating in the reaction. Such a simplified picture is in contrast to the mechanism involving both π bonds as outlined by us earlier.[2-4]

To determine the relative importance of the two factors considered, namely (a) control by electron delocalization in the reacting species *vs.* (b) correlation between double bond excitation energy and involvement in the reaction, we selected 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene (**5**). Application of our qualitative valence bond mechanism for the di-π-methane rearrangement to this compound (*i.e.*, **5**) leads to species **6**. If electron delocalization is the controlling factor, the ring-fission process represented by arrows a should predominate. In contrast, if the extent to which the two chromophoric π systems are perturbed from the ground-state wave function is controlling, then no selectivity would be expected, since the excited state energies of the diphenylvinyl and styryl moieties are essentially identical (*vide infra*).



5



6

Additionally, we wished to investigate the relationship of excited state rate constants to structure in the di-π-methane transformation. Although this is common

---

(1) For paper LXI of this series, note H. E. Zimmerman and T. W. Fletchner, *J. Amer. Chem. Soc.*, **93**, 7170 (1971).

(2) H. E. Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969).

(3) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6259, 6267 (1970).

(4) (a) The first formulation of the di-π-methane rearrangement was in the case of barrelene to semibulvalene.[4b] Note also ref 2 and H. E. Zimmerman, *Angew. Chem.*, **81**, 45 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **89**, 3932 (1967); (c) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969).

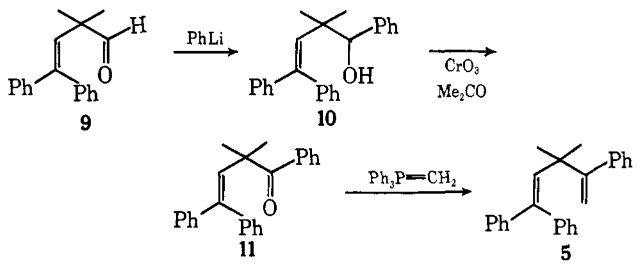
(5) The di-π-methane rearrangement can involve participation between any two π systems in principle. Givens was the first to note that the rearrangement of β,γ-unsaturated ketones to cyclopropanes is general and termed this an oxa-di-π-methane rearrangement.[6]

(6) R. S. Givens, *Chem. Commun.*, 1164 (1969).

in ketone photochemistry, such rate constants have not been generally available in photochemical rearrangements of unsaturated hydrocarbons.

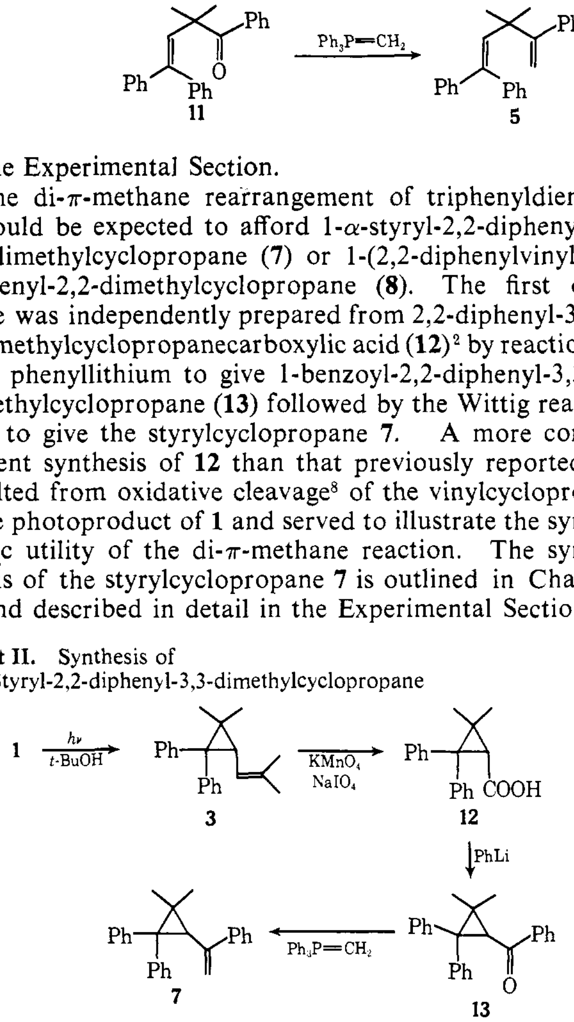
Synthesis of Reactant and Potential Rearrangement Products. 1,1,4-Triphenyl-3,3-dimethyl-1,4-pentadiene (**5**) was synthesized starting with 2,2-dimethyl-4,4-diphenyl-3-butenal (**9**).[3a,7] This was converted to the triphenyldiene **5** by reaction with phenyllithium, oxidation, and the Wittig reaction of the resulting olefinic ketone **11**. This is summarized in Chart I and detailed in the Experimental Section.

Chart I. Synthesis of 1,1,4-Triphenyl-3,3-dimethyl-1,4-pentadiene



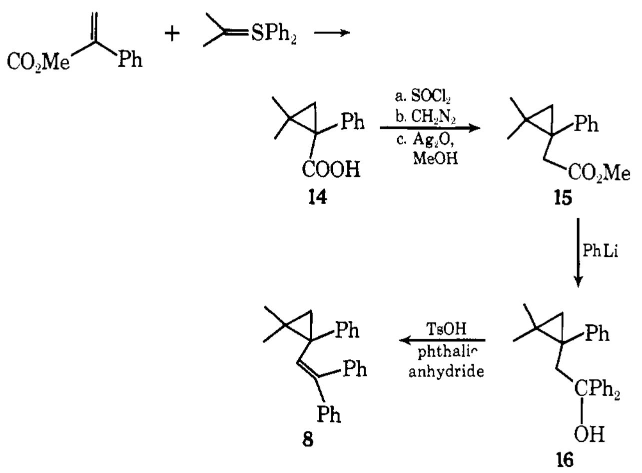
The di-π-methane rearrangement of triphenyldiene **5** would be expected to afford 1-α-styryl-2,2-diphenyl-3,3-dimethylcyclopropane (**7**) or 1-(2,2-diphenylvinyl)-1-phenyl-2,2-dimethylcyclopropane (**8**). The first of these was independently prepared from 2,2-diphenyl-3,-3-dimethylcyclopropanecarboxylic acid (**12**)[2] by reaction with phenyllithium to give 1-benzoyl-2,2-diphenyl-3,3-dimethylcyclopropane (**13**) followed by the Wittig reaction to give the styrylcyclopropane **7**. A more convenient synthesis of **12** than that previously reported[2] resulted from oxidative cleavage[8] of the vinylcyclopropane photoproduct of **1** and served to illustrate the synthetic utility of the di-π-methane reaction. The synthesis of the styrylcyclopropane **7** is outlined in Chart II and described in detail in the Experimental Section.

Chart II. Synthesis of 1-α-Styryl-2,2-diphenyl-3,3-dimethylcyclopropane



The alternative di-π-methane product **8** was prepared beginning with the reaction of methyl α-phenylacrylate with diphenylsulfonium isopropylide to give methyl 1-phenyl-2,2-dimethylcyclopropanecarboxylate following the general method of Corey.[9] Subsequent saponification, Arndt–Eistert homologation, phenyllithium reaction of the ester product **15**, and dehydration of the tertiary carbinol **16** gave the desired diphenylvinylcyclopropane **8**. This sequence is shown in Chart III and is detailed in the Experimental Section.

Chart III. Synthesis of 1-(2,2-Diphenylvinyl)-1-phenyl-2,2-dimethylcyclopropane



Exploratory Photolyses. The irradiation of 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene (**5**) was found to give primarily (73%) one product, a vinylcyclopropane. This product was found to be the previously synthesized 1-α-styryl-2,2-diphenyl-3,3-dimethylcyclopropane (**7**). This was one of the two *a priori* di-π-methane rearrangement products. The alternative product which had been considered possible, namely 1-(2,2-diphenylvinyl)-1-phenyl-2,2-dimethylcyclopropane (**8**), was found by nmr inspection to be missing. This was done both by checking the initially isolated reaction mixture and scrutinizing the residues left after isolation of the major product **7**.

In order to make certain that the nonobserved diphenylvinylcyclopropane **8** was not simply being consumed under reaction conditions, the photolysis of this compound was tried. Although this photochemistry itself is of intrinsic interest, it is presently sufficient to note that the diphenylvinylcyclopropane **8** gave rise to photochemistry not observed in the present study of the photolysis of 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene. Thus, it can be safely concluded that of the two possible di-π-methane rearrangement products, only the styrylcyclopropane product **7** was formed.

Reaction Efficiency and Multiplicity. Quantum yield determinations were made using our "black box" apparatus[10] which utilized three filter solutions, a parabolic reflector, a G.E. AH6 1000-W high-pressure lamp, and 5.5-in. diameter cells. With ferrioxalate actinometry a quantum yield of $\phi = 0.008 \pm 0.0008$ was obtained in *tert*-butyl alcohol.

Benzophenone sensitization in *tert*-butyl alcohol was used under conditions where energy transfer was certain to be efficient from the benzophenone triplet but not from the singlet. The triphenyldiene **7** proved to be unreactive, showing that the independently generated triplet of 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene did not give rise to the di-π-methane rearrangement observed on direct irradiation, leaving the excited singlet identified as the reacting species.

Determination of Excited State Rate Constants. With the quantum yield now available, a comparison of the efficiency of the presently studied reaction with those studied earlier was possible and promised to be interesting. However, a more meaningful comparison involved the reaction rate constants for the excited

---

(7) M. Julia and M. Baillarge, *Bull. Soc. Chim. Fr.*, 734 (1966).

(8) E. von Rudloff, *Can. J. Chem.*, **33**, 1714 (1955).

(9) E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 3912 (1967).

(10) H. E. Zimmerman and G. Jones, II, *ibid.*, **92**, 2753 (1970).

Table I. Excited State Rate Constants and Quantum Yields

Compound	ϕ_f	ϕ_r	k_f, sec^{-1}	k_{dt}, sec^{-1}	k_r, sec^{-1}	k_d, sec^{-1}
$Ph_2C{=}CH_2$	300×10^{-5}		2.6×10^8	8.7×10^{10}		8.7×10^{10}
Triphenyldiene[a]	31.8×10^{-5}	0.008	4.4×10^8	1.38×10^{12}	1.11×10^{10}	1.37×10^{12}
Tetraphenyldiene[b]	7.6×10^{-5}	0.08	7.4×10^8	9.74×10^{12}	7.78×10^{11}	8.96×10^{12}

[a] Refers to 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene. [b] Refers to 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene.

state rearrangement. Ideally, the rate constants for all processes leading from the excited singlet were desired. These included the rate of rearrangement (k_r), the rate of fluorescence (k_f), and the rate of energy dissipation by all nonradiative processes (k_d).

It turns out that from expressions 1 and 2 for the quantum yields of fluorescence and reaction, one can in principle obtain all of the desired rate constants provided that ϕ_f, ϕ_r, and one of the rate constants are known. Here k_f is the specific rate of fluorescence, k_r

$$\phi_f = k_f/(k_f + k_r + k_d) = k_f/(k_f + k_{dt}) \qquad (1)$$

$$\phi_r = k_r/(k_f + k_r + k_d) \qquad (2)$$

is the rate of singlet rearrangement, k_d is the sum of specific rates of singlet radiationless decay (including intersystem crossing), and k_{dt} corresponds to the sum of all radiationless modes of singlet excited state destruction.

It is seen that eq 1 and 2 may be combined to give

$$\phi_r/\phi_f = k_r/k_f \qquad (3)$$

and eq 1 may be expressed in terms of k_{dt} to give

$$k_{dt} = k_f(1 - \phi_f)/\phi_f \qquad (4)$$

The values of k_f may be estimated from eq 5,[11] relating the integrated extinction coefficient for the lowest singlet absorption band to the rate of fluorescence from the lowest energy singlet excited state

$$k_f = \frac{\bar{\nu}_m{}^2 \int \epsilon(\bar{\nu}) d\bar{\nu}}{3.5 \times 10^8} \qquad (5)$$

where $\bar{\nu}_m$ is the mean frequency, in wave numbers, of the absorption band and $\epsilon(\bar{\nu})$ is the extinction coefficient. These integrated extinction coefficients were obtained from the ultraviolet spectra in cyclohexane. Overlap of the 0–0 portion of the absorption and emission peaks indicated that the correct absorption bands were being selected. The values of the integrated extinction coefficients utilized are given in the Experimental Section, and the values of k_f obtained for the model compound 1,1-diphenylethylene, 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**17**),[2] and the presently studied 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene are given in Table I. The isoenergetic relation of the chromophores was shown by the essential identity of wavelength and peak shape of the ultraviolet spectra of these compounds.

One approach to determining the sum of the rate constants in the denominator of eq 1 and 2 involves the measurement of biacetyl fluorescence in the presence of the molecule being studied. The very sensitive method of du Bois[12] was used. This method uses the relation

$$\lim_{[D] \to 0} (F_A/F_A{}^0) = 1 + \frac{\epsilon_D}{\epsilon_A}\left(\frac{k_q \tau_D}{1 + k_q \tau_D [A]}\right)[D] \qquad (6)$$

where A refers to biacetyl, D refers to a singlet energy donor, the ϵ's are the appropriate extinction coefficients at the excitation wavelength, k_q is the quenching rate constant, τ_D is the donor's singlet lifetime in the absence of biacetyl, and F_A and $F_A{}^0$ are the fluorescence intensities of biacetyl in the presence and absence of sensitizer, respectively.

Although it proved possible to repeat the work of du Bois in detecting transfer from both biphenyl ($k_{dt} + k_f = 1.33 \times 10^8$ sec^{-1}) and toluene ($k_{dt} + k_f = 2.32 \times 10^8$ sec^{-1}), no transfer could be detected from diphenylethylene, nor from **5**, or **17**. This test sets a lower limit on $k_{dt} + k_f$ as 10^9 sec^{-1}, since fivefold less efficient energy transfer would have been detected but was not. With the values of k_f in Table I, k_{dt} is seen to be minimally 10^{10} sec^{-1} for the three compounds in question.

A more successful approach to getting the desired rate constants was derived from the use of eq 3 (*vide supra*). Quantum yields of fluorescence, as required by this approach, were determined relative to that of 1,1-diphenylethylene which is known as $\phi_f = 0.003$.[13] This method seemed reliable, since the emission curves for 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene and 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene were essentially identical in shape and wavelength with that of 1,1-diphenylethylene, giving rise to no monochrometer and phototube response problems. Additionally, this provided further evidence for the isoenergetic nature of the chromophores. The fluorescence quantum yields obtained are included in Table I.

The solution of eq 3 was now possible using: (a) the measured values of the fluorescence quantum yields; (b) the previously obtained rates of fluorescence (note Table I and previous discussion); and (c) the quantum yields for the di-π-methane rearrangement. This solution afforded the desired singlet excited state rate constants (*i.e.*, the k_r's).

Finally, since $k_{dt} = k_r + k_d$, it was possible to solve for the k_d's, the operational singlet decay rates. These are included in Table I.

Interpretative Discussion. The first point to note is the occurrence of the di-π-methane reaction mechanism, thus adding still another illustration of the generality of the process. Secondly, the directionality is that expected on the basis of minimization of electron localization along the excited state potential energy surface.

It is seen in Chart IV that path a avoids the odd-electron localization on a nonphenyl bearing center and retains the benzhydryl delocalization present in species **6**, while in path b, this delocalization is lost. Thus, we have in hand still another excited state reaction where the course is determined by the tendency of the excited state to minimize its energy. This energetic control of photochemical reactions has been previously noted to

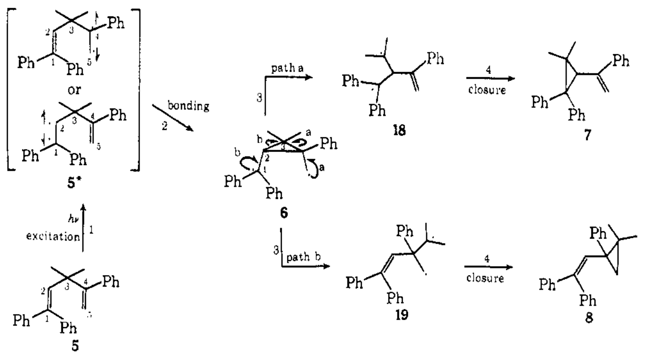
---

[11] T. Förster, "Fluorezenz Organischer Verbindungen," Vandenhoech und Ruprech, Gottingen, 1951.

[12] J. T. du Bois and M. Cox, *J. Chem. Phys.*, **38**, 2536 (1963).

[13] I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, p 89.

Chart IV. Delocalization as Controlling the Di-π-methane Rearrangement of 1,1,5-Triphenyl-3,3-dimethyl-1,4-pentadiene

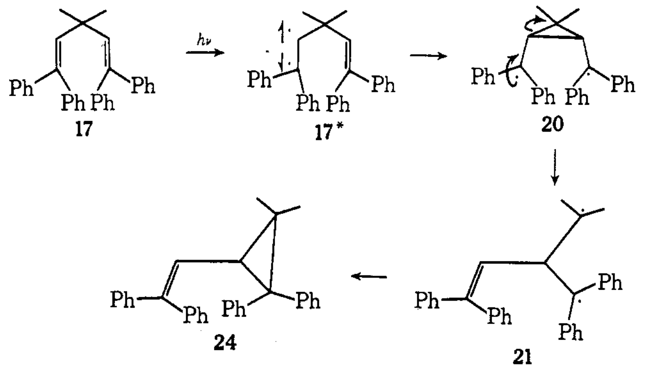


be important in a large number of photochemical reactions.[4a,14]

Again, the generalization made by us earlier[2,3] that acyclic di-π-methanes prefer rearrangement *via* the singlet excited state and that the triplets tend to be unreactive toward this transformation has proven correct.

One of the most striking results is the 70-fold greater rate of excited singlet rearrangement of the tetraphenyldiene **17** compared with the triphenyldiene **5**. The relative rates of reaction differ even more dramatically than suggested by comparison of the quantum yields. It is noted, from comparison of the mechanism of Charts IV and V, that if ring opening of the vinyl–vinyl bridged species **6** and **20** is rate limiting, then the rate of reaction of singlet **5*** should be greater than **17***, since more delocalization is lost in the latter case. This is contrary to observation. However, if bridging of the excited singlets **5*** and **17*** is rate limiting, one can see that the tetraphenyldiene singlet **17*** should be faster than the triphenyldiene singlet **5*** since more delocalization is gained. This does fit observation and seems the preferred alternative.[15]

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



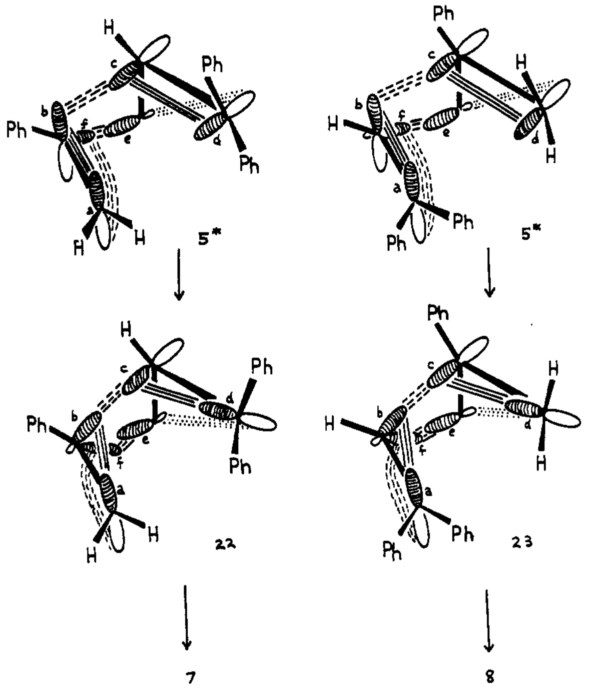


Figure 1. Orbital array changes during the di-π-methane rearrangement. Dashed lines, new bonds forming; ≡, bonds breaking; dotted lines, new bond forming slowly.

The correlation of these excited state rate constants with structural reasoning using relatively simple formulations of the reacting excited state is encouraging. Success in correlating singlet excited state reactivity with excited state structural modification and substitution hence seems a promising direction for effort. This finds parallel in our finding of similar correlations of excited state rate constants and substitution in the case of triplets.[16]

Finally, it is of interest to inspect the molecular orbital formulation of the di-π-methane process and to consider its ability to accommodate the reaction directionality. Figure 1 gives the basis orbital change during the reaction for the two potential rearrangements. We note that the reaction involves three increases in overlap during the reaction, namely: b–c, a–f, and d–e. The first corresponds to bond formation between vinyl C-2 and -4 (as in structure **5***). The second overlap is the process regenerating the π bond between C-1 and -2 or C-4 and -5 (as in species **6**). Finally, the last (*i.e.*, d–e) corresponds to product three-ring formation (as from species **18** to give styrylcyclopropane product **7**). Although the evidence is that these processes are concerted, nevertheless, *a priori*, one would not expect them to proceed exactly concomitantly.[17] Of these three processes, one would expect the three-ring formation (*i.e.*, overlap d–e) to proceed most gradually. In fact, the oversimplified qualitative valence bond picture in Chart IV suggests that, in the absence of the stereochemical evidence we presented earlier,[3b] this process might have been reasonably formulated as a totally separate step. Furthermore, evidence has been advanced (*vide supra*) that vinyl–vinyl bonding

---

(14) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **83**, 4486 (1961); **84**, 4527 (1962).

(15) The precise interpretation of k_r and k_d depends on whether or not the bridged species is in dynamic equilibrium with the unbridged singlet excited state. If bridging is reversible then any decay of the bridged species to reactant ground state will lead to enhancement of k_d as measured. If bridging is not reversible, any such decay merely serves to lower the measured k_r. In this latter event, the k_r's derived will be "effective k_r's indicating the effective reactivity of excited state in giving product. That is, k_r (actual) = sk_r where s is a success factor measuring the probability of the vinyl–vinyl bridged species going onward to product rather than reverting to ground-state reactant. In any case, the k_r (actual) values can be expected again to favor the tetraphenyldiene **17** relative to the triphenyldiene **5**, since the ratio of rates of reversion of bridged species **6** and **20** to ground state should be less than the ratio of rates of three-ring opening in the forward. This conclusion is based on the expectation that a highly exothermic process in which two odd electrons interact to form two new π bonds with loss of a single σ bond should be less selective as a function of structure than a process in which one biradical is formed from another.

(16) H. E. Zimmerman and N. Lewin, *J. Amer. Chem. Soc.*, **91**, 879 (1969).

(17) One must remember that "concerted" means that the subportions of the reaction proceed overlapping in time. These subprocesses must not, however, necessarily proceed equally strongly as a function of time.

is rate limiting, and an appreciable approach to product geometry at this early stage seems unreasonable.

To the extent that d–e overlap is indeed weak in the rate-limiting portion of the reaction, we find a linear array of six orbitals: e–f–a–b–c–d, an array roughly isoelectronic with hexatriene. Clearly, due to the nature of the highest bonding and lowest antibonding MO's of hexatriene, in which the terminal atoms are most heavily weighted, a hexatriene-like excited state will be most stabilized by extra phenyl substitution at the *end* of the linear array.[18] This means that the excited species having the orbital array of **22** and terminal phenyl groups will be of lower energy than the counterpart having the array of **23** which has alternative phenyl substitution.

In conclusion, one may note that the di-π-methane rearrangement promises to be an extraordinarily general process and the controlling features seem to be developing in accord with the picture originally presented.

Experimental Section[19]

1,4,4-Triphenyl-2,2-dimethyl-3-buten-1-ol. To a solution of phenyllithium prepared from 7.85 g (0.050 mol) of bromobenzene and 0.700 g (0.010 g-atom) of freshly cut lithium in 40 ml of anhydrous ether was added a solution of 10.236 g (0.041 mol) of 2,2-dimethyl-4,4-diphenyl-3-butenal[3,7] in 45 ml of anhydrous ether. The addition was made under nitrogen and at a rate sufficient to cause gentle reflux. The mixture was then stirred at reflux for 0.5 hr, cooled, and poured onto ice. The ether layer was washed with water, dried, and concentrated giving 13.51 g (98%) of a viscous, yellow oil. This material was sufficiently pure for use in the next step, but could be further purified by chromatography on silica gel eluting wtih 5–10% ether in hexane. Such treatment yields the pure carbinol as a colorless vsicous oil. The spectral data were: nmr (CCl_4) τ 2.70–2.80 (m, 15 H, arom), 3.84 (s, 1 H, vinyl), 5.50 (br s, 1 H, methine), 7.96 (br s, 1 H, hydroxyl), 9.08 (s, 3 H, methyl), 9.19 (s, 3 H, methyl); ir ($CHCl_3$) 2.79 μ (hydroxyl); mass spectrum (70 eV, direct inlet) showed molecular ion at *m/e* 328.19; calcd for $C_{24}H_{24}O$: 328.19.

Anal. Calcd for $C_{24}H_{24}O$: C, 87.76; H, 7.36. Found: C, 88.05; H, 7.55.

1,4,4-Triphenyl-2,2-dimethyl-3-buten-1-one. To a stirred solution of 5.531 g (0.017 mol) of 1,4,4-triphenyl-2,2-dimethyl-3-buten-1-ol in 100 ml of reagent acetone was added 6.0 ml of a 4 *N* solution of CrO_3 in 20% H_2SO_4. The mixture was then stirred at room temperature for an additional 0.5 hr. The acetone was then removed under reduced pressure; the residue was diluted with water, and was ether extracted. The extracts were washed first with saturated bicarbonate solution, and then with water. After drying and concentration *in vacuo*, a residue of 5.236 g remained. This material was chromatographed on a 3 × 110 cm column slurry packed with silica gel in CCl_4. Elution was with 500 ml each of 5, 10, 20, 30, 40, and finally 1.5 l. of 50% $CHCl_3$ in CCl_4; 500-ml fractions were collected. Fractions 6–8 contained 4.432 g (81%) of a colorless, viscous oil which crystallized upon standing and proved to be the desired ketone. This material was recrystallized from methanol to give a waxy solid, mp 54–55°. The spectral data were: nmr ($CDCl_3$) τ 2.00–2.15 (m, 2 H, arom), 2.49–2.92 (m, 13 H, arom), 3.50 (s, 1 H, vinyl), 8.58 (s, 6 H, CH_3); ir (CCl_4) 5.94 μ (C=O). Mass spectrum (70 eV, direct inlet) showed molecular ion at *m/e* 325.995; calcd for $C_{24}H_{22}O$: 326.000.

Anal. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.28; H, 6.77.

1,1,4-Triphenyl-3,3-dimethyl-1,4-pentadiene. To a stirred suspension of 6.27 g (18.4 mmol) of methyltriphenylphosphonium bromide in 100 ml of anhydrous ether was added, under nitrogen over 1 hr, 8.17 ml of a 2.25 *M* solution of *n*-butyllithium in hexane. To the resulting orange solution was added 3.002 g (9.2 mmol) of 1,4,4-triphenyl-2,2-dimethyl-3-buten-1-one dissolved in 20 ml of anhydrous ether. The stirred mixture was refluxed under nitrogen for 14 hr. The mixture was then poured into 300 ml of cold pentane and filtered through Celite. The filtrate was washed with water, dried, and concentrated leaving a residue which partially crystallized on standing. This material was chromatographed on a 2 × 50 cm column slurry packed with silica gel in 6% ether in hexane. Elution was with 6% ether in hexane and 500-ml fractions were taken. Fractions 1 and 2 combined contained 2.579 g (87%) of a colorless, crystalline solid which was characterized as the desired diene. This material was recrystallized from 95% ethanol, mp 51–52°. The spectral properties were as follows: nmr (CCl_4) τ 2.80–2.88 (m, 15 H, arom), 3.88 (s, 1 H, vinyl), 4.91 (d, *J* = 1.3 Hz, 1 H, vinyl), 5.17 (d, *J* = 1.3 Hz, 1 H, vinyl), 8.92 (s, 6 H, methyl); uv $\lambda_{max}^{cyclohexane}$ 250 nm (ϵ 16,200); ir (CCl_4) 11.04 μ.

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.76; H, 7.32.

2,2-Diphenyl-3,3-dimethylcyclopropanecarboxylic Acid.[3a] This material was prepared in 85% yield by permanganate-periodate oxidation of 1,1-dimethyl-2,2-diphenyl-3-(2-methylpropenyl)cyclopropane according to the method of Zimmerman and Pratt.[3a]

1-Benzoyl-2,2-diphenyl-3,3-dimethylcyclopropane. To a stirred solution of 0.794 g (0.003 mol) of 2,2-diphenyl-3,3-dimethylcyclopropanecarboxylic acid in 50 ml of anhydrous ether was added 5.6 ml of 2.14 *M* solution of phenyllithium in 7:3 benzene–ether. The addition was made under nitrogen at 0°. The mixture was stirred under nitrogen at 0° for an additional 1 hr and was then hydrolyzed by addition of water. The aqueous layer was acidified with 5% sulfuric acid and was ether extracted; these extracts, after drying and concentration, yielded 0.181 g (23%) of the starting acid. The ether layer, after drying and concentration, gave 1.316 g of an oily residue which was chromatographed on a 2 × 60 cm silica gel column slurry placked with 5% ether in hexane. Elution was with 5% ether–hexane and 250-ml fractions were collected. Fractions 2 and 3 gave 0.195 g of a mixture of components which were not characterized. Fractions 4, 5, and 6 gave 0.565 g (75.5% based on consumed acid) of a colorless, oily residue which was identified as the desired 1-benzoyl-2,2-diphenyl-3,3-dimethylcyclopropane. The spectral properties were as follows: nmr (CCl_4) τ 1.90–2.10 (m, 2 H, arom), 2.50–2.90 (m, 13 H, arom), 6.72 (s, 1 H, cyclopropyl CH), 8.51 (s, 3 H, cyclopropyl methyl), 8.78 (s, 3 H, cyclopropyl methyl); ir (CCl_4) 5.97 μ (C=O).

For the 2,4-dinitrophenylhydrazone derivative, mp 249–251° dec, the mass spectrum (70 eV direct inlet) showed a molecular ion at *m/e* 506.223; calcd for $C_{30}H_{26}N_4O_4$: 506.224.

1-α-Styryl-2,2-diphenyl-3,3-dimethylcyclopropane. To a stirred suspension of 1.23 g (0.0035 mol) of methyltriphenylphosphonium bromide in 25 ml of anhydrous ether was added, over 15 min under nitrogen, 1.54 ml of a 2.25 *M* hexane solution of *n*-butyllithium. To the resulting solution was added a solution of 0.565 g (0.0017 mol) of 1-benzoyl-2,2-diphenyl-3,3-dimethylcyclopropane in 15 ml of anhydrous ether, and the mixture was refluxed for an additional hr. The mixture was then cooled, filtered through Celite, and concentrated. The residue was filtered through alumina with 2% ether in hexane and the filtrate was concentrated *in vacuo* to give 0.430 g (77%) of product as a colorless, viscous oil. The spectral properties were as follows: nmr (CCl_4) τ 2.50–3.16 (m, 15 H, arom), 4.81 (d, *J* = 0.8 Hz, 1 H, vinyl), 5.63 (t, *J* = 0.8 Hz, 1 H, vinyl), 7.58 (d, *J* = 0.8 Hz, 1 H, cyclopropyl CH), 8.68 (s, 3 H, cyclopropyl methyl), 8.83 (s, 3 H, cyclopropyl methyl); uv $\lambda_{max}^{95\%\ EtOH}$ 230 nm (ϵ 20,000); ir (CS_2) 8.98, 9.75, 11.16 μ.

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.55; H, 7.52.

1-Phenyl-2,2-dimethylcyclopropanecarboxylic Acid. A suspension of diphenylisopropylsulfonium iodide in 450 ml of dry 1,2-dimethoxyethane was prepared according to the method of Corey[8] from 60.00 g (0.199 mol) of diphenylethylsulfonium fluoroborate, 0.146 mol of lithium diisopropylamide (from 15.75 ml of diisopropylamine and 73 ml of a 2.0 *M* solution of butyllithium in hexane), dissolved in 75 ml of dimethoxyethane, 12 ml of CH_2Cl_2, and 21.2 g (0.149 mol) of methyl iodide. To this was added another 0.146 mol of lithium diisopropylamide in 75 ml of anhydrous dimethoxyethane. This entire procedure was carried out at −80° and under nitrogen.[9] To the stirred, −80° solution of diphenylsulfonium isopropylide thus produced was added 17.689 g (0.109 mol) of methyl α-phenylacrylate.[20] The addition was made with

---

(18) This is really just another way of saying that 1-phenylhexatriene has a lower energy singlet than 3-phenylhexatriene. Also, note that interaction of the single phenyl group will be roughly equivalent for either mode of reaction since it appears at atoms 2 or 5 in the hexatriene-like system.

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

(20) A. McKenzie and J. K. Wood, *J. Chem. Soc.*, 828 (1919).

vigorous stirring under nitrogen. The stirred mixture was allowed to warm to room temperature over 4 hr after which it was filtered. The filtrate was concentrated *in vacuo*, dissolved in 250 ml of a 10% solution of potassium hydroxide in methanol, and refluxed for 8 hr. The resulting mixture was cooled, concentrated under vacuum, and diluted with water, and was ether extracted. The aqueous layer was acidified to congo red with 15% hydrochloric acid solution and was ether extracted. These ether extracts were dried and concentrated to give 18.764 g (90.5%) of cyclopropyl acid. This material was conveniently recrystallized from pentane, mp 104.5–106.5°. The spectral properties were: nmr (CCl_4) τ −3.00 (br s, 1 H, carboxyl), 2.80 (m, 5 H, arom), 8.33 (d, J = 4.5 Hz, 1 H, cyclopropyl), 8.69 (s, 3 H, methyl), 8.90 (d, J = 4.5 Hz, 1 H, cyclopropyl), 9.20 (s, 3 H, methyl); ir (CCl_4) 3.00–4.40 μ (br, COOH), 5.94 μ (C=O).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.55; H, 7.15.

Methyl 1-Phenyl-2,2-dimethylcyclopropaneacetate. To 5.567 g (0.0294 mol) of 1-phenyl-2,2-dimethylcyclopropanecarboxylic aicd was added 25.0 ml of thionyl chloride freshly distilled from unboiled linseed oil. The solution was stirred at room temperature for 3 hr after which the excess thionyl chloride was removed by distillation. The dark residue was distilled at reduced pressure, bp 70° (1 mm), to give 3.808 g of a clear mobile liquid. This material was dissolved in 40 ml of anhydrous ether and added to a solution of 0.033 mol of diazomethane in 300 ml of dry ether. The addition was made at 0° with vigorous stirring, followed by stirring at 0° for 1 hr more, after which the ether and excess diazomethane were removed in a stream of nitrogen. The yellow residue was dissolved in 25 ml of ether, filtered, and concentrated leaving 3.854 g of a yellow oil. This material was dissolved in 8 ml of anhydrous methanol and added to a well-stirred suspension of 1 g of freshly prepared silver oxide in 100 ml of anhydrous methanol which had been preheated to 40°. The temperature was then raised to 80° and nitrogen evolved smoothly. When the rate of nitrogen evolution decreased, an additional amount of silver oxide was added, this process being repeated until gas evolution had ceased completely. At this point, a small aliquot of the reaction mixture did not liberate nitrogen upon acidification with 10% HCl. A total of 3.628 g of silver oxide was required. The mixture was then filtered and concentrated leaving a deep-red, oily residue which was dissolved in 150 ml of 10% methanolic potassium hydroxide and refluxed for 7 hr. The resulting mixture was concentrated under vacuum and diluted with water, and was ether extracted. The aqueous layer was acidified to congo red with 15% hydrochloric solution and was ether extracted. The extracts were dried and concentrated leaving 1.905 g of an oil which crystallized upon standing. This material was dissolved in 15 ml of ether and added to a stirred solution of 0.033 mol of diazomethane in 300 ml of ether at 0°. After addition, the ether and excess diazomethane were removed in a stream of nitrogen, and the residue (1.627 g) was chromatographed on a 3 × 100 cm column slurry packed with silicic acid in 4% ether–hexane. Elution was with 4% ether–hexane, and 40-ml fractions were collected. Fractions 73–108 gave, after concentration, 0.757 g (19.3% overall) of the desired methyl ester. The spectral data were as follows: nmr (CCl_4) τ 2.80 (s, 5 H, arom), 6.52 (s, 3 H, carbomethoxy methyl), 7.41 (center of AB quartet, J = 16 Hz, $\Delta\delta$ = 3 Hz, 2 H, acyclic methylene), 8.68 (s, 3 H, cyclopropyl methyl), 9.02 (d, J = 7 Hz, 1 H, cyclopropyl CH), 9.19 (s, 3 H, cyclopropyl methyl), 9.30 (d, J = 7 Hz, 1 H, cyclopropyl CH); ir ($CHCl_3$) 5.87 μ (C=O).

Anal. Calcd for $C_{13}H_{16}O_2$:[21] C, 76.44; H, 7.90. Found: C, 76.79; H, 8.17.

1,1-Diphenyl-2-(1-phenyl-2,2-dimethylcyclopropane)ethanol. To a solution of phenyllithium prepared from 0.087 g (0.0125 g-atom) of lithium and 0.975 g (0.00625 mol) of bromobenzene in 25 ml of anhydrous ether was added 0.531 g (0.00243 mol) of methyl 1-phenyl-2,2-dimethylcyclopropaneacetate dissolved in 10 ml of anhydrous ether. After cooling and addition of water, the aqueous layer was ether extracted and the combined ether extracts were dried and concentrated leaving 0.820 g of the crystalline carbinol. The material was recrystallized from hexane: mp 82–84°. The spectral data were: nmr (CCl_4) τ 2.59–3.21 (m, 15 H, arom), 6.99 (d, A part of AB quartet, J = 14 Hz, 1 H, acyclic CH_2), 7.5 (d, B part of AB quartet, J = 14 Hz, 1 H, acyclic CH), 8.20 (s, 1 H, hydroxyl), 8.73 (s, 3 H, cyclopropyl methyl), 9.28 (d, J = 5 Hz, 1 H, cyclopropyl HCH), 9.47 (s, 3 H, cyclopropyl methyl), 9.67 (d, J = 5 Hz, 1 H, cyclopropyl HCH); ir (CCl_4) 2.80 μ (O—H).

Anal. Calcd for $C_{25}H_{26}O$: C, 87.67; H, 7.65. Found: C, 87.53; H, 7.79.

1-(2,2-Diphenylvinyl)-1-phenyl-2,2-dimethylcyclopropane. A solution of 0.081 g (0.235 mmol) of 1,1-diphenyl-2-(1-phenyl-2,2-dimethylcyclopropane)ethanol, 0.074 g (0.50 mmol) of phthalic anhydride, and 3.0 mg of *p*-toluenesulfonic acid in 20 ml of anhydrous benzene was refluxed for 1 hr. The benzene was removed under vacuum and the residue was chromatographed on a 2 × 26 cm column slurry packed with silicic acid in 1% ether–hexane. Elution was with 1% ether–hexane, and 100-ml fractions were collected. Fractions 2 and 3 gave, after concentration, 0.073 g (96%) of the desired crystalline vinylcyclopropane. The material was recrystallized from 95% ethanol: mp 83–84°. The spectral data were: nmr (CCl_4) τ 2.67–3.13 (m, 15 H, arom), 3.50 (s, 1 H, vinyl), 8.73 (s, 3 H, cyclopropyl methyl), 9.12 (d, J = 5.5 Hz, 1 H, cyclopropyl methylene), 9.31 (s, 3 H, cyclopropyl methyl), 9.73 (d, J = 5.5 Hz, 1 H, cyclopropyl methylene); uv $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 255 nm (ϵ 14,000).

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.54; H, 7.45.

Direct Photolysis of 1,1,4-Triphenyl-3,3-dimethyl-1,4-pentadiene. Product Isolation. A solution of 0.516 g (1.59 mmol) of 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene in 500 ml of *tert*-butyl alcohol was purged with purified nitrogen[22] for 1 hr before and during photolysis. The irradiation was carried out for 1.6 hr using a 450-W Hanovia medium-pressure mercury lamp with a Corex cut-off filter, all in a water-cooled immersion well. Removal of solvent under vacuum gave 0.525 g of a clear yellow-brown oil. This material was chromatographed on a 100 × 3.5 cm column slurry packed with Florisil in hexane. Elution was with hexane, and 40-ml fractions were collected. The eluent was scanned at 250 nm prior to collection. Fractions 61–80 contained 0.193 g of a crystalline material which was identical with the starting diene (nmr, mixture melting point, ir). Fractions 117–172 contained 0.182 g of noncrystallizing oil which was comprised mainly of a material whose nmr matched the nmr of the previously synthesized 1-α-styryl-2,2-diphenyl-3,3-dimethylcyclopropane; *vide supra*. Fractions 132–142 were combined and separately examined by nmr and ir. Nmr (CCl_4) showed that this material was comprised of better than 90% of the above vinylcyclopropane: τ 2.50–3.16 (m, 15 H, arom), 4.81 (d, J = 0.8 Hz, 1 H, vinyl) 5.63 (t, J = 0.8 Hz, 1 H, vinyl), 7.58 (d, J = 0.8 Hz, 1 H, cyclopropyl methine); ir (CS_2) 8.98. 9.75, 11.16 μ. A total of 0.375 g (71%) of material was recovered from this column. Additionally, it should be noted that neither in the crude, unchromatographed photolysis mixture nor in any of the chromatographic subfractions was it possible to detect any 1-(2,2-diphenylvinyl)-1-phenyldimethylcyclopropane (**8**) (*vide supra*) or its photolysis products by nmr.

Direct Photolysis of 1,1,4-Triphenyl-3,3-dimethyl-1,4-pentadiene. Quantitative Product Determination. A solution of 0.367 g (1.134 mmol) of 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene in 500 ml of *tert*-butyl alcohol was purged with purified nitrogen for 1 hr before and during irradiation. The solution was irradiated in the apparatus described above for 3 hr. After solvent removal *in vacuo*, 0.373 g of oily residue remained. The absolute quantities of diene remaining and vinylcyclopropane formed were determined by nmr spectroscopy using freshly distilled *p*-dioxane as an internal standard. For the determination of the remaining diene, the area of the vinyl singlet at τ 3.88 was compared to the area of the singlet from 5.00 μl of *p*-dioxane. The vinylcyclopropane was determined by comparison of the τ 5.63 resonance with the dioxane resonance. The results showed that 0.913 mmol of diene remained, or that 0.221 mmol of diene had been consumed by the photolysis, and that 0.160 mmol of the styrylcyclopropane was formed. Thus, at 17% conversion, the styrylcyclopropane was formed in 73% yield. The accuracy of the assay was found to be ±5% by checking known solutions and in agreement with results using other characteristic peaks.

Determination of Quantum Yields for the Di-π-methane Rearrangement of 1,1,4-Triphenyl-3,3-dimethyl-1,4-pentadiene. General Procedure. In quantum yield determinations, the photolyses were performed in the "black box" apparatus which has been previously described.[3,10] The filters employed in the direct photolysis were those described by Zimmerman and Pratt,[3a] and consisted of three solutions contained in a triple-chambered cell. The solu-

---

[21] Elemental analysis was performed on the crystalline acid rather than the methyl ester.

[22] L. Meites, *Anal. Chem.*, 20, 984 (1948).

tions were: (a) 2 M nickel sulfate hexahydrate in 5% sulfuric acid; (b) 5% sulfuric acid saturated with cobalt sulfate heptahydrate at 25° and diluted with 25% of its volume with 5% sulfuric acid; (c) 2 $\times$ 10^{-4} M $BiCl_3$ in 10% hydrochloric acid. This combination gave a transmission maximum at 273 nm and was opaque above 305 nm and below 250 nm. In the sensitized runs, the filter solutions employed were: (a) 26.3 g of nickel sulfate hexahydrate in 1 l. of 10% sulfuric acid; (b) 112.5 g of cobalt sulfate heptahydrate in 1 l. of 10% sulfuric acid; (c) 22.5 g of stannous chloride dihydrate in 1 l. of 10% hydrochloric acid. This combination gave a transmission maximum at 345 nm (38%) and was opaque above 385 nm and below 315 nm. Potassium ferrioxalate actinometry[23] was employed. The actinometry procedure was modified considerably from that used in the past. The "black box" was fitted with a 45° 2 $\times$ 2 $\times$ $^1/_{16}$ in. quartz plate beam slitter situated between the filter cells and the photolysis cell. A small fraction of the filtered light was reflected into a side cell situated in a compartment perpendicular to the main beam. Prior to and after each photolysis, a splitting ratio was determined by filling both front and rear compartments of the main cell[3a] and the side cell with potassium ferrioxalate, irradiating, and determining the light absorbed by each solution. During the actual photolysis, the side cell was filled with potassium ferrioxalate solution as was the rear compartment of the main cell. From the known splitting ratio and the energy absorbed in the side cell during the photolysis together with the energy absorbed in the rear compartment of the main cell, the total energy absorbed by the solution being irradiated was determined. In all cases, the solvent employed was *tert*-butyl alcohol freshly distilled from calcium hydride. In the sensitized runs, benzophenone was employed as the sensitizer. For 1 hr prior to and during photolysis a stream of purified nitrogen[23] was bubbled through the stirred solutions.

Direct Quantum Yields. 1,1,4-Triphenyl-3,3-dimethyl-1,4-pentadiene was irradiated in dilute *tert*-butyl alcohol solution with appropriately filtered light; *vide supra*. All runs were made in 750 ml of solvent. After photolysis, the solvent was removed *in vacuo* below 40°. The product was subjected to reverse-phase liquid–liquid partition chromatography on a 3.5 $\times$ 200 cm polystyrene beads column eluting with a 2:1 solution of methanol–cyclohexane.[2] The eluent was scanned at 250 nm and 40-ml fractions were collected. The product vinylcyclopropane was eluted along with small quantities of a minor product in fractions 77–99 which overlapped the unreacted diene eluted in fractions 86–117. The vinylcyclopropane-containing fractions were combined and the quantity of vinylcyclopropane was determined by nmr analysis using *p*-dioxane as an internal standard. Data for the individual runs are listed below as follows: weight of starting diene, energy absorbed by photolysis solution, number of moles of 1-α-stryryl-2,2-diphenyl-3,3-dimethylcyclopropane formed, and quantum yield.

Run 1. Starting diene (0.362 g, 1.12 mmol), 1.69 mEinsteins, vinylcyclopropane formed too small to measure, $\phi < 0.10$.

Run 2. Starting diene (0.365 g, 1.13 mmol), 11.10 mEinsteins, 8.76 $\times$ 10^{-2} mmol of vinylcyclopropane, $\phi = 0.0079$.

Sensitized Quantum Yield. A solution of 5.008 g (27.6 mmol) of benzophenone and 0.365 g (1.13 mmol) of 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene in 750 ml of *tert*-butyl alcohol was irradiated at 315–385 nm (*vide supra*) under nitrogen after thoroughly purging with nitrogen for 1 hr. The benzophenone absorbed >99.99% of the light under these conditions. A total of 9.13 mEinsteins of light was absorbed. After concentration *in vacuo* the photolysate was chromatographed as above on polystyrene beads. The benzophenone, fractions 32–51, was cleanly separated from the hydrocarbon material, fractions 77–127. The hydrocarbon peak was divided into five parts, each containing 10 sequential fractions. Each part was separately concentrated *in vacuo* and examined by nmr spectroscopy. Only unreacted diene was seen to be present. A total of 0.356 g of diene was recovered (97.5%). Thus, the quantum efficiency of sensitized vinylcyclopropane formation was $\phi = 0.000$.

Singlet Lifetime Determination *via* the Sensitization of Biacetyl Fluorescence.[12] General Procedure. The fluorescences of solutions containing a constant amount of biacetyl (0.003 M) and a varying amount of the compound under study were measured using an Aminco-Kiers spectrophosphorimeter, and the biacetyl fluorescence, λ_{max} 460 nm, was recorded. Cyclohexane solvent was purified by distillation and filtration through a silver nitrate impregnated alumina column;[25] this was shown to be free of fluorescent impurities to within the limits of detection by the instrument. The excitation wavelength was 260 nm. The slit arrangement employed in this study was as follows: entrance slits, 3, 2 mm; exit slits, 2, 3 mm; photomultiplier slit, 3 mm.

In the event that biacetyl fluorescence enhancement was observed in the solutions containing sensitizer, the intensity at the biacetyl maximum relative to that in the absence of sensitizer was plotted as a function of sensitizer concentration. From the limiting slope (as sensitizer concentration approaches zero), the measured extinction coefficients of biacetyl and sensitizer at the excitation wavelength, and the bimolecular quenching constant (taken to be the diffusion constant, $k_q = 8.0 \times 10^9$ l. M^{-1} sec^{-1}, in cyclohexane at 25°),[12] the lifetime of the sensitizer was calculated using eq 6 (*vide supra*). The results of these measurements are presented in Table II.

Table II. Sensitization of Biacetyl Fluorescence By Various Sensitizers[a]

Sensitizer	Concn, M	Intensity of biacetyl fluorescence at maximum[b]	τ_s, sec
Toluene[c]	...	10.2	4.3×10^{-9}
	2×10^{-4}	11.8	
	4×10^{-4}	13.1	
	5×10^{-4}	13.9	
Biphenyl[d]	...	90	7.5×10^{-9}
	0.5×10^{-5}	100	
	1.0×10^{-5}	111	
	1.5×10^{-5}	123	
	2.0×10^{-5}	137	
1,1-Diphenylethylene[e]	...	12.0	Too small to measure
	1×10^{-6}	11.6	
	5×10^{-5}	11.0	
	1×10^{-5}	10.3	
Triphenyldiene[f]	...	12.0	Too small to measure
	1×10^{-6}	11.4	
	1×10^{-5}	10.5	
Tetraphenyldiene[g]	1.11×10^{-6}	11.6	
	1.11×10^{-5}	9.9	

[a] Biacetyl $\epsilon_{260\ nm}$ 14.5. [b] Measured in arbitrary units. [c] Toluene $\epsilon_{260\ nm}$ 250. [d] Biphenyl $\epsilon_{260\ nm}$. [e] 1,1-Diphenylethylene $\epsilon_{260\ nm}$ 9000. [f] 5$\epsilon_{260\ nm}$ 14,000. [g] 17 $\epsilon_{260\ nm}$ 23,000.

Determination of Fluorescence Quantum Yields. The fluorescence spectra of 1,1-diphenylethylene, 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene, and 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene were measured in cyclohexane solution. The concentration was 0.001 M in each case. All slits were set at 3 mm and excitation was at 267 nm. Each compound showed a fluorescence maximum at 310 nm, and the shapes of the emission envelopes were all essentially identical. The fluorescence quantum yields were computed from the known value for 1,1-diphenylethylene and the intensity at the maximum relative to 1,1-diphenylethylene. The results are presented in Table III.

Table III. Calculation of Fluorescence Quantum Yields

Compound	Intensity at maximum (arbitrary units)	ϕ_f
1,1-Diphenylethylene	1300	0.003
Triphenyldiene	138	0.000318
Tetraphenyldiene	33	0.000076

Calculation of Fluorescence Rate Constants. Equation 5 (*vide supra*) was used to compute these values. The integral $\int \epsilon(\bar{\nu})d\bar{\nu}$

---

(23) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (*London*), **235,** 518 (1956).

Table IV. Calculation of Fluorescence Rate Constants

Compound	ϵ_{max}	$\tilde{\nu}_m$, cm^{-1}	$\Delta\tilde{\nu}_{1/2}$, cm^{-1}	k_f, sec^{-1}
1,1-Diphenylethylene	1.19×10^4	4.0×10^4	4.8×10^3	2.6×10^8
Triphenyldiene	1.63×10^4	4.0×10^4	5.90×10^3	4.4×10^8
Tetraphenyldiene	2.34×10^4	3.95×10^4	7.0×10^3	7.3×10^8

was approximated as the band height at the maximum, ϵ_{max}, multiplied by the width of the band at half-height. The pertinent values are listed in Table IV.

Acknowledgment. Support of this research by National Institutes of Health Grant No. GM 07487 and the National Science Foundation is gratefully acknowledged. A. A. B. also acknowledges partial support by an NIH postdoctoral fellowship.

Competitive Photochemical Pathways in the Di-π-methane Rearrangement. Exploratory and Mechanistic Organic Photochemistry. LXIII[1,2]

Howard E. Zimmerman,* Peter Hackett, Daniel F. Juers, John M. McCall, and Barbara Schröder

Contribution from the Department of Chemistry, the University of Wisconsin, Madison, Wisconsin 53706. *Received September 30, 1970*

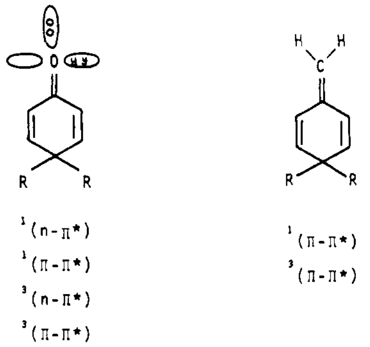
Abstract: The photochemistry of the methylene analogs of the 4,4-diphenyl- and 4,4-dimethylcyclohexadienones was investigated. Direct irradiation of 1-methylene-4,4-dimethyl-2,5-cyclohexadiene afforded 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene in superficial analogy to the dienone type A process. However, in contrast to the dienone situation, the reaction was shown to proceed *via* the singlet, and the triplet was found to give no unimolecular rearrangement. Additionally, the 0.0029 quantum yield suggested a mechanism different than the nearly unit efficiency dienone process. 1-Methylene-4,4-diphenyl-2,5-cyclohexadiene differed in that phenyl migration interceded, affording the cis and trans stereoisomers of 2-methylene-5,6-diphenylbicyclo[3.1.0]-3-hexene. The reaction was highly stereoselective with the trans product predominating 36:1. This reaction, too, was found to utilize the singlet excited state and the triplet was unreactive. The singlet reaction efficiency was enhanced by the availability of the phenyl migration process which had a quantum yield of 0.135 (*vs.* $\Phi = 0.0029$ for the dimethyltriene). The bicyclic dienes from these rearrangements were found to be primary photoproducts which gave rise to further photochemistry. Mechanistic aspects of the reactions are discussed including: the relation to ketone photochemistry, comparison with acyclic di-π-methane rearrangements, and the efficiencies of different available competitive processes.

A number of complex photochemical rearrangements of carbonyl compounds have been given mechanistic explanation using the electronics of the n–π* excited state as a basis.[3,4] The availability of this n–π* excited state derives from the presence of the p_y (nonbonding) orbital at the carbonyl oxygen.

The intriguing possibility of studying molecules lacking this p_y orbital and therefore lacking an n–π* excited state suggested itself. Such a molecule would have available only π–π* excited states and its photochemistry would define the behavior of these states.

Since 4,4-disubstituted cyclohexadienones have been the subject of intensive study in these laboratories,[4] the methylene analogs were selected for the present study.[5] Specifically, 1-methylene-4,4-diphenyl-2,5-cyclohexadiene (**2**) and 1-methylene-4,4-dimethyl-2,5-cyclohexadiene (**1**) were selected. Note Chart I.

Chart I. Excited States Available to Dienones and Methylene Analogs



---

[1] For paper LXII of the series, see H. E. Zimmerman and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 3646 (1971).

[2] For a preliminary communication describing a portion of the present work, note H. E. Zimmerman, P. Hackett, D. Juers, and B. Schröder, *ibid.*, **89**, 5973 (1967).

[3] (a) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); (b) H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969); (c) H. E. Zimmerman, *Science*, **153**, 837 (1966).

[4] (a) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **83**, 4486 (1961); **84**, 4527 (1962); (b) H. E. Zimmerman and J. S. Swenton, *ibid.*, **86**, 1436 (1964); **89**, 906 (1967); (c) H. E. Zimmerman and G. Jones, II, *ibid.*, **92**, 2753 (1970); **91**, 5678 (1969).

[5] Very recently we have reported on the photochemistry of the methylene analog of 4,4-diphenylcyclohexenone; see H. E. Zimmerman and G. E. Samuelson, *ibid.*, **89**, 5971 (1967); **91**, 5307 (1969).

Zimmerman, et al. / Photochemical Pathways in the Di-π-methane Rearrangement