acid was heated to 70°, and isobutylene was bubbled through the mixture until vpc analysis showed almost all **6** to have reacted (*ca.* 20 min). The product was washed with water and then with 3 *N* sodium hydroxide solution. It was dried and evaporated to give 1.2 g (4.7 g, 92%) of **17** as a yellow viscous oil, which showed only one significant peak in the vpc. An analytical sample was obtained by vpc on column B (220°, R_t 21 min). Its ir and nmr spectra were identical with those of the crude product. *Anal.* Calcd for $C_{18}H_{22}O$: C, 85.0; H, 8.72. Found: C, 85.0; H, 8.62. The nmr spectrum had peaks at 8.70 (s, 9 H), 8.15 (s, 3 H), 6.23 (s, 2 H), 3.50 (d, J = 9.0 cps, 1 H), 3.13 (d, partially hidden), 3.00 (broad singlet, 5 H).

Rearrangement of Dienone 10. A solution of dienone **10** (0.30 g) in 10 ml of 1.0 *N* HCl in methanol was allowed to stand at room temperature for 24 hr. The uv spectrum of the solution then showed the absence of any unreacted **10**. The reaction was worked up as usual to give 0.3 g of yellow oil. Vpc analysis of the product on column A, starting at 120° with the temperature rising at 4°/min, showed the presence of four peaks with retention times of 1.8 (2.7), 2.0 (1.5), 3.4 (6.4), and 20.6 (5.1) min. The four components were isolated by preparative vpc on column B at 225°, and identified as benzyl methyl ether, benzyl chloride, 2,6-dimethylphenol, and an unidentified phenol, presumably either **13** or **14**. The phenol had nmr peaks at τ 7.92 and 7.97 (s, totaling 6 H), 6.33 (s, 2 H), 6.21 (s, 1 H), 3.2–3.5 (m, *ca.* 2 H), and 3.02 (broad absorption, 5 H). *Anal.* Calcd for $C_{15}H_{16}O$; C, 84.9; H, 7.60. Found: C, 84.7; H, 7.51.

Kinetics. Samples of dienones **1** and **7** were dissolved in 0.50 *N* HCl in 80% aqueous methanol, using concentrations such that the uv spectrum of the solutions could be measured directly, without further dilution. The solutions were kept in a constant-temperature bath at 25.8 ± 0.1°, and samples pipeted out at intervals for uv analysis. The disappearance of the absorption maxima at 308 mμ was followed. The reaction rates of **1** and **7** in the absence of acid were also followed. **1** was found to be unchanged after 14 hr in the absence of acid, while **7** disappeared at the same rate in neutral and in acid solution.

Acknowledgments. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and The National Science Foundation for grants in partial support of this work.

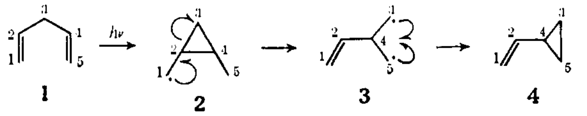
Unsymmetrical Substitution and the Direction of the Di-π-methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry. LVI[1]

Howard E. Zimmerman and Albert C. Pratt

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received January 22, 1970*

Abstract: 1,1-Diphenyl-3,3,5-trimethyl-1,4-hexadiene (**5**) was synthesized in order to study the effect of substitution on the direction of the di-π-methane rearrangement. Direct irradiation of diene **5** gave 1,1-dimethyl-2,2-diphenyl-3-(2-methylpropenyl)cyclopropane (**6**), whose structure was established by its spectral properties and by degradation. No 1,1,2,2-tetramethyl-3-(2,2-diphenylvinyl)cyclopropane (**7**) was formed (<3%). The absence of vinylcyclopropane **7** was not due to its destruction, either in a process leading to the observed product vinylcyclopropane (**6**) or in reactions giving further products. This was established by the near perfect mass balance for the direct photolysis and by the photochemical behavior of independently synthesized vinylcyclopropane **7**. It was found that the singlet excited state of diene **5** undergoes the di-π-methane rearrangement smoothly and cleanly with a quantum efficiency of 0.097 while T_1 rearranges only with difficulty (ϕ = 0.008). The photochemistry of the vinylcyclopropanes **6** and **7** was explored. The photochemistry of **6** involved two types of carbene fission. In contrast the irradiation of vinylcyclopropane **7** led to a unique rearrangement involving three-ring fission and methyl migration to give 1,1-diphenyl-4,5,5-trimethyl-1,3-hexadiene (**13**) as the major product.

Previously we have described a number of examples of the di-π-methane rearrangement[2–6] and have noted that the rearrangement is general, occurring whenever two π moieties are bonded to one sp^3 hybridized carbon atom. Thus far we have advanced tentative correlations between molecular structure and the multiplicity of the reacting excited state. Also, in the case of bicyclic systems, we have described initial efforts toward determining which two π moieties bridge preferentially when more than two bridging processes are *a priori* possible.[3,5]



1 **2** **3** **4** (1)

In the present investigation we have turned our attention to another facet of the problem, namely the direction of rearrangement in an unsymmetrically substituted divinylmethane. Thus, for example, if carbon atoms 1 and 5 of the system in eq 1 were differently substituted, after bridging to give species **2** there would exist not only the possibility of bond 2–3 fission as shown but also bond 3–4 cleavage. Different vinylcyclopropanes would then be potential products. We felt it of practical interest and also of importance in understanding the electronic details of the mechanism

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[1] (a) For the preliminary communication note H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **92**, 1407 (1970); (b) for paper LII of the series note H. E. Zimmerman and H. Iwamura, *ibid.*, **92**, 2015 (1970); for LV see H. E. Zimmerman and G. A. Epling, *ibid.*, **92**, 1411 (1970).

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

[3] H. E. Zimmerman and C. O. Bender, *ibid.*, **91**, 7516 (1969).

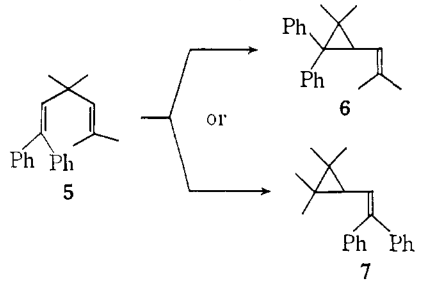
[4] (a) H. E. Zimmerman and G. E. Samuelson, *ibid.*, **91**, 5307 (1969); (b) H. E. Zimmerman, P. Hackett, D. F. Juers, and B. Schröder, *ibid.*, **89**, 5973 (1967).

[5] H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 6096 (1969).

[6] H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969).

to investigate the factors controlling the molecular pathway chosen.

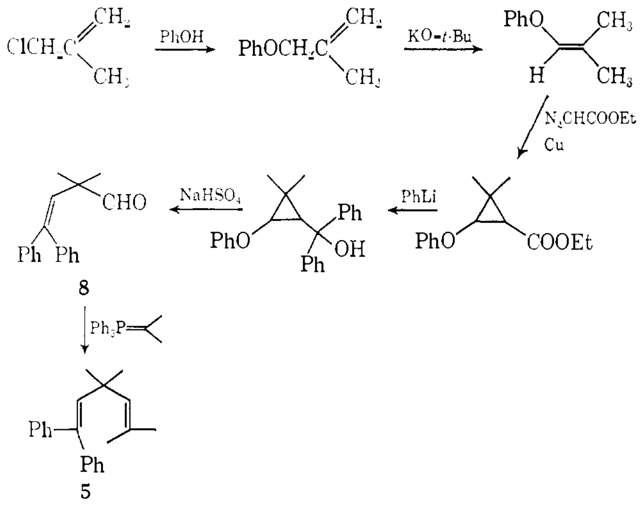
The molecule selected for study was 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene (**5**). The two possible vinylcyclopropane products are 1,1-dimethyl-2,2-diphenyl-3-(2-methylpropenyl)cyclopropane (**6**) and 1,1,-2,2-tetramethyl-3-(2,2-diphenylvinyl)cyclopropane (**7**); *cf.* eq 2. It was felt that aryl substitution at carbon-1 with only alkyl substitution at carbon-5 would provide a test of the extent of buildup of free valences with intervention of radicaloid species such as **2**.



(2)

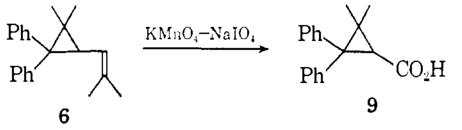
Synthetic Aspects. The requisite diene **5** was synthesized by a Wittig reaction of isopropylidenetriphenylphosphorane with the known[7] aldehyde, 2,2-dimethyl-4,4-diphenyl-3-butenal (**8**); this is depicted in Chart I and described in the Experimental Section.

Chart I. Synthesis of 1,1-Diphenyl-3,3,5-trimethyl-1,4-hexadiene (**5**)



Exploratory Photochemistry and Product Structure Elucidation. Initial photochemical studies were carried out with a 450-W medium-pressure immersion apparatus and Corex filter cutting off light below 270 mμ. Irradiation of 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene (**5**) in *t*-butyl alcohol under nitrogen was found to afford one product, mp 77°, cleanly and without detectable by-products. From 2.00 g of reactant diene **5** there was obtained in 3 hr 1.52 g of the photoproduct (**6**) and 0.55 g of recovered starting material.

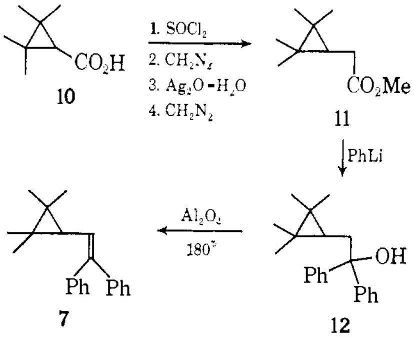
The product structure was strongly suggested by the nmr spectrum. The vinyl region consisted of a doublet of multiplets at τ 5.27 (J = 9 cps) corresponding to a single proton. Coupled to this (J = 9 cps) was a τ 7.93 methine doublet. Additionally, there were four three-proton absorptions above τ 8.0. Two of these were singlets, τ 8.88 and 8.97, which could be assigned to nonequivalent cyclopropyl methyl groups. The remaining two were doublets, τ 8.14 (J = 1.2 cps) and 8.28 (J = 1.0 cps), and were assignable to nonequivalent allylic methyls both of which were coupled to the vinyl proton. Structure **6** was indicated on the basis of this nmr information and this assignment was confirmed by oxidation of the photoproduct by the method of von Rudloff[8] to the known 2,2-dimethyl-3,3-diphenylcyclopropanecarboxylic acid (**9**).

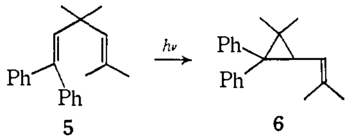


(3)

Furthermore, synthesis of the other vinylcyclopropane **7** was achieved as outlined in Chart II. Arndt–Eistert chain lengthening of 2,2,3,3-tetramethylcyclopropanecarboxylic acid (**10**)[9] followed by esterification of the product with diazomethane gave methyl 2,2,3,3-tetramethylcyclopropaneacetate (**11**). Treatment of the ester (**11**) with excess phenyllithium in ether provided 1,1-diphenyl-2-(2,2,3,3-tetramethylcyclopropane)ethanol (**12**). Dehydration of this carbinol by heating with alumina at 180° resulted in 1,1,2,2-tetramethyl-3-(2,2-diphenylvinyl)cyclopropane (**7**). Comparison of the vinylcyclopropane (**7**) with the photoproduct (**6**) confirmed the fact that they were indeed different.

Chart II. Synthesis of 1,1,2,2-Tetramethyl-3-(2,2-diphenylvinyl)cyclopropane (7)





(4)

Hence the reaction can be seen to be highly selective with preferential formation of the isopropylidenecyclopropane product (**6**). This is formulated in eq 4.

Results

Mechanistic Studies. Reaction Efficiency and Multiplicity. In view of the remarkable facility and selectivity of the photochemical reaction observed under preparative conditions, it was of considerable interest to determine the efficiency of the reaction. Additionally, since now a number of di-π-methane systems are being studied in our laboratories, knowledge of the reaction efficiency would allow comparison with other di-π-methane systems and hopefully correlation with structure.

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

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

(9) A. P. Meschcheryakov and I. E. Dolgii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 931 (1960); *Chem. Abstr.*, 54, 24436*d* (1960).

Quantum yield studies were carried out in the "black box" apparatus used in our laboratories for some years and described briefly in earlier papers.[10] This utilized a high-pressure AH6 lamp in a parabolic reflector and a ramp containing three successive filter-solution cells and finally reaction and actinometric cells.

Quantum yields were run with and without benzophenone sensitizer and the results are listed in Table I; also the details are given in the Experimental Section. It may be seen that the reaction is indeed a relatively efficient one. This accords with the initial exploratory observation that the reaction was facile. In general, reactions with near 10% efficiencies seem to have a high probability of being relatively uncomplex and therefore synthetically useful.

Table I. Quantum Yield Studies on 1,1-Diphenyl-3,3,5-trimethyl-1,4-hexadiene (**5**)

Run[a,b]	Sensitizer, M[c]	Quantum yield	Mass balance, %
1	None	0.102 ± 0.007	99.2
2	None	0.093 ± 0.007	99.2
3	0.076	0.008 ± 0.002	98.4
4	0.077	0.008 ± 0.002	97.1

[a] Concentrations of reactant diene were in the range of 0.0025–0.0050 M. [b] Light capture by product was not significant and photolysis of product was not occurring under reaction conditions in direct runs. [c] Benzophenone, concentration adjusted to absorb over 98% of the light.

Secondly, the runs with benzophenone absorbing the light were designed with a low enough reactant concentration that benzophenone singlets would not survive long enough to allow singlet energy transfer but with a high enough reactant concentration to allow interception of essentially all of the benzophenone triplet molecules by reactant.[11] Such collisions should be relatively efficient in view of the 68.8 kcal/mol energy of triplet benzophenone and the much lower (*ca.* 62 kcal/mol) triplet energy expected[12] for reactant diene **5**.

That triplet transfer was indeed successful was established by the finding that the benzophenone–benzhydrol triplet reaction,[15] when run under similar concentration conditions, was quenched by addition of diene **5**. Thus, quenching of the benzophenone–benzhydrol reaction (note Table II) showed triplet energy transfer to be at least 93% efficient in sensitized runs. In these runs, however, no vinylcyclopropane product could be detected (note runs 3 and 4, Table I).

Vinylcyclopropane Photochemistry. Because of the possibility that the structurally isomeric vinylcyclopropanes **6** and **7** might actually be involved in the photochemistry of 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene (**5**) in more subtle ways than **6** merely being a nonreacting product and **7** being a potential but unobserved product, the photochemistry of these two compounds was investigated.

Table II. Evidence for Energy Transfer from Benzophenone Triplet to 1,1-Diphenyl-3,3,5-trimethyl-1,4-hexadiene (**5**)

Run[a]	Wt, g (concn, M), of diene **5**	Wt, g (concn, M), of benzophenone	Wt, g (concn, M), of benzhydrol	Wt, g, of benzpinacol produced
1	None	6.000 (0.144)	2.000 (0.047)	2.027
2	0.504 (0.008)	6.000 (0.144)	2.000 (0.047)	0.132

[a] Irradiations carried out in preparative apparatus using Pyrex filter for 22 min.

Thus, in the case of 1,1,2,2-tetramethyl-3-(2,2-diphenylvinyl)cyclopropane (**7**) it was *a priori* possible that this compound was not encountered because of efficient further reaction once formed. Because of the excellent mass balance and absence of other products such reactions would have to be reconversion to reactant diene **5** or a less structurally plausible but not impossible[16] reaction leading to the observed 1,1-dimethyl-2,2-diphenyl-3-(2-methylpropenyl)cyclopropane (**6**). Actually, one might expect to find evidence of the presence of vinylcyclopropane **7** or intermediates[16] leading to it if **7** were formed; nevertheless, examination of the photochemistry of **7** proved most convincing.

On irradiation, under conditions similar to those employed in the exploratory photolysis of diene (**5**), 1,1,2,2-tetramethyl-3-(2,2-diphenylvinyl)cyclopropane (**7**) yielded a product, mp 68°. Although there was some evidence for some by-product, formation of this compound appeared to represent the primary reaction course. The ultraviolet spectrum showed a maximum at 299 mμ (ϵ 24,700) and a shoulder at 225 (15,135), very reminiscent of 1,1-diphenylbutadiene moieties.[17] The nmr spectrum indicated the presence of nine methyl hydrogens absorbing at τ 9.01 as a sharp singlet and an AB quartet attributable to adjacent vinyl hydrogens, the quartet being centered at τ 3.60 with the upfield half slightly split by coupling to a methyl group. Corresponding to this coupling was an allylic methyl group at τ 8.14 appearing as a doublet with $J = 1.5$ cps. These data suggested 1,1-diphenyl-4,5,5-trimethyl-1,3-hexadiene (**13**) as the photoproduct. The validity of this conclusion was established by synthesis as delineated in Chart III. This bizarre rearrangement (note eq 5) is discussed in more detail in the interpretative section below. Since neither the product 1,1-diphenyl-4,5,5-trimethyl-1,3-hexadiene (**13**) obtained from direct photolysis of 1,1,2,2-tetramethyl-3-(2,2-diphenylvinyl)cyclopropane (**7**) nor vinylcyclopropane **7** itself were observed in the original photolysis of 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene (**5**), the conclusion that vinylcyclopropane **7** is not a product of photolysis of the diene **5** is confirmed.

Photolysis of 1,1-dimethyl-2,2-diphenyl-3-(2-methylpropenyl)cyclopropane (**6**) led to less interesting

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(10) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966).

(11) Proper selection of such conditions is discussed in ref 10.

(12) Styrene, which should provide a relatively good upper limit for the energy of diene **5**, has been found by Evans[13] and Hammond[14] to have a triplet energy of 62 kcal/mol.

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

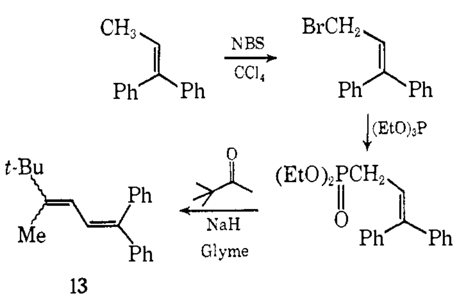
(14) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 43, 2129 (1965).

(15) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

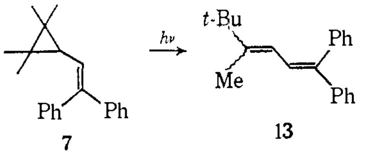
(16) One potential route would involve a vinylcyclopropane to cyclopentene conversion of **7** to 3,3-diphenyl-4,4,5,5-tetramethylcyclopentene followed by a subsequent cyclopentene to vinylcyclopropane rearrangement to **6**.

(17) Note ref 10 where maxima at 231 (ϵ 15,390), 236 (15,390), and 294 mμ (22,800) were reported for *cis*-6,6-diphenyl-3,5-hexadienoic acid and maxima at 277 (ϵ 14,250) and 290 mμ (24,600) were recorded for *trans*-6,6-diphenyl-3,5-hexadienoic acid.

Chart III. Synthesis of 1,1-Diphenyl-4,5,5-trimethyl-1,3-hexadiene (13)

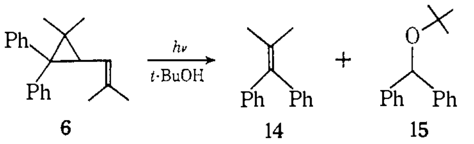


photochemistry. However, the products again proved to be ones which were not observed in the photolysis of diene 5 and no reversion to diene 5 was encountered.



(5)

Irradiation of photovinylcyclopropane 6 in *t*-butyl alcohol afforded 1,1-diphenyl-2-methylpropene (14) and benzhydryl *t*-butyl ether (15); note eq 6. The structures of these products were verified by simple syntheses (note Experimental Section).



(6)

Interpretative Discussion

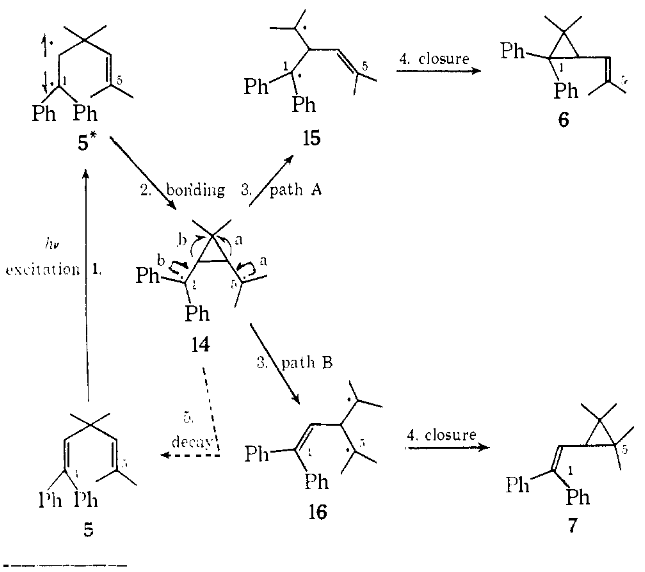
The Di-π-methane Rearrangement of 1,1-Diphenyl-3,3,5-trimethyl-1,4-hexadiene (5). The first point to be made is that the present rearrangement of 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene (5) to 1,1-dimethyl-2,2-diphenyl-3-(2-methylpropenyl)cyclopropane (6) provides still another example of the di-π-methane rearrangement.[2–6] Actually, acyclic examples are less plentiful than cyclic and bicyclic ones, and this is therefore a comforting addition. The complete generality of the di-π-methane to π-cyclopropane rearrangement seems thus more firmly established.

Secondly, in order to discuss the molecular details of the reaction, the matter of reaction multiplicity is important. From the evidence presented above, it is seen that the present di-π-methane rearrangement occurs efficiently *via* the singlet excited state. Thus, when the lowest triplet T_1 is generated artificially by benzophenone sensitization, the reaction does proceed but only very inefficiently. This leaves the singlet as the most reasonable candidate for the excited state responsible for the reaction.[18] The finding that the singlet of 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene (5) is the excited species responsible for the present reaction is not unreasonable. (1) Intersystem crossing of hydrocarbons tends to be relatively slow[15] and hence the probability of finding singlet reactions tends to be greater for hydrocarbon reactants than, *e.g.*, for ketones. (2) The low reactivity of the triplet of diene 5 is not totally unexpected and has precedent in the three unconstrained di-π-methane systems[2,4] where triplet reactivity has been investigated. This lack of reactivity seems to derive from the presence of a free rotor capable of dissipating triplet energy. In the present instance rotation about the excited diphenylethylene, and possibly the isopropylidene, double bonds is a mode of energy dissipation in the triplet. It appears that energy dissipation by free rotation about excited π bonds is more characteristic of triplets than singlets, although such a generalization is necessarily tentative.[19]

Thirdly, the most dramatic result requiring discussion is the complete selectivity exhibited in the photochemistry of 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene (5) wherein, of the two possible vinylcyclopropanes 6 and 7 (note eq 2) which might *a priori* be formed, only 1,1-dimethyl-2,2-diphenyl-3-(2-methylpropenyl)cyclopropane (6) was encountered. In the Results section, it has been pointed out that this selectivity is a result of kinetic preference and not due to either interconversion of products or selective destruction of the nonobserved isomer.

The molecular forces controlling this selectivity require discussion. We note a disinclination for the electronically unexcited double bond to be destroyed in the di-π-methane transformation. This conclusion actually is merely a restatement of the experimental observation and is a deduction made possible by the reaction course. However, it remains to rationalize this predilection. In simplest terms, reference to Chart IV reveals that in the observed reaction pathway

Chart IV. Valence Bond Considerations Controlling Reaction Selectivity



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(18) Actually, the present evidence merely excludes T_1 as the species primarily responsible and the choice of S_1 rather than, *e.g.*, T_2 is based on analogy with our earlier di-π-methane studies[2,4] where the use of a triplet sensitizer with sufficient energy to generate T_2 led to no reaction.

(19) The present observation is consistent with our previous findings[2,4] and contrasts with the facile and efficient di-π-methane rearrangement found earlier for the bicyclic and hence constrained di-π-methane systems.[3,5,6] However, that double bond rotation is possible for *both* singlets and triplets derives from the efforts of Saltiel,[20] Fischer,[21] and Hammond[22] and their coworkers.

(20) J. Saltiel, O. C. Zafiriou, E. D. Megarity, and A. A. Lamola, *J. Amer. Chem. Soc.*, 90, 4759 (1968).

(21) D. Gegiou, K. A. Muszkat, and E. Fischer, *ibid.*, 90, 3907 (1968).

(22) G. S. Hammond, *et al.*, *ibid.*, 86, 3197 (1964).

(A), fission of 1,4-biradical **14** gives species **15** which has a heavily delocalized odd electron center at carbon-1 while in the alternative pathway (B) species **16** has relatively localized electron density centered at carbon-5.

It should be recognized that the separate steps in Chart IV are depicted separately for convenience and actually represent individual molecular changes, *i.e.*, bonds broken and formed, during the rearrangement. Chart IV therefore is not meant to imply lack of concertedness. Thus, while stabilization in structures **15** and **16**, as these species are developing, is a controlling factor, nevertheless there is no evidence that these are indeed energy minima and intermediates rather than mere points along a concerted potential energy surface.

If one does picture the reaction as potentially concerted, he may envisage an orbital system as shown in Figure 1. This figure deals only with the orbitals intimately involved in the mechanism and shows which overlap is originally present and which develops along the reaction coordinate. The orbital array has been used previously[2] in another connection, namely to show that the excited-state process is symmetry allowed.

However, the representation may be used to allow a prediction of the site of substitution which will minimize the energy of the reacting species. We note that not only the stepwise process represented in eq 1 and Chart IV but also a reasonable view of the concerted process predict bond 1–3 (*i.e.*, orbital overlap d–e; Figure 1) to lag behind the other processes shown. This is reasonable since bonding to the saturated sp^3 hybridized carbon-3 of reactant diene **5** would not be expected without prior intervention of the other steps of eq 1 and Chart IV. To the extent that overlap d–e is neglected, the parent orbital system is a linear array of six overlapping orbitals: e–f–a–b–c–d.[23] This system is then crudely isoelectronic with hexatriene. Clearly, minimization of the excited state energy is by substitution of the aryl group at the terminus of the six orbital system (*i.e.*, at carbon-1 or d) rather than at a central position (*i.e.*, at carbon-5 or a).[25] The former corresponds to the reaction as observed and the latter to the unobserved reaction course. This is most simply put as linear conjugation with a terminal phenyl group being preferred over cross-conjugation in the excited state.

One final point deserves comment, namely the remarkably similar quantum efficiency (*i.e.*, 0.097) in the present molecule, which has one diphenylethylene moiety, compared with the quantum yield of the di-π-methane rearrangement of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**17**) having two diphenylethylene moieties[26] and an efficiency of 0.080[2]. This requires that the ratio of the excited state rearrangement rate to the excited state decay rate be the same for the two molecules. Two rationales are reasonable. One is that the two molecules have very similar rates of singlet excited state rearrangement and also comparable excited state decay rates.[27] The alternative is that the ratios are similar despite different k_r's and k_d's.

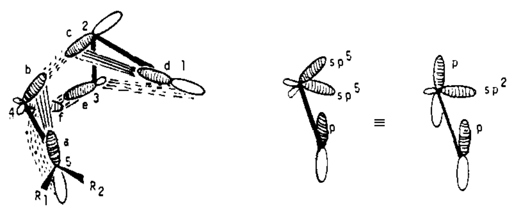

Figure 1. Orbital array during the di-π-methane rearrangement: ≡, bonds forming; ═, bonds breaking; —, bonds unchanged; ▨, + lobes in basis set; ☐, − lobes in basis set.

Although a definitive choice cannot be presently made, the latter may be seen to be particularly reasonable. Reference to Chart IV shows that both the forward reaction and the decay process of 1,4-biradical **14** (processes 3 and 5, respectively) should be affected in the same direction by replacement of the two terminal *i.e.*, C-5) methyl groups by phenyl substituents. Both of these processes are three-ring fission reactions of the cyclopropylcarbinyl radical to allylcarbinyl variety and their rates should depend on the availability of high electron density at carbon-5, an electron availability diminished by phenyl substitution.

Interpretative Discussion of the Vinylcyclopropane Photochemistry. The different behavior of the two vinylcyclopropanes, 1,1-dimethyl-2,2-diphenyl-3-(2-methylpropenyl)cyclopropane (**6**) and 1,1,2,2-tetramethyl-3-(2,2-diphenylvinyl)cyclopropane (**7**), where **6** gives rise to carbene fission and **7** affords rearrangement product 1,1-diphenyl-4,5,5-trimethyl-1,3-hexadiene (**13**), is of interest. However, since multiplicity studies have not yet been run, discussion of this aspect is limited to noting that in **6** the excitation energy must be heavily localized in the cyclopropyl phenyl groups while in **7** the diphenylvinyl moiety is the most easily excited portion of the molecule. Hence the strikingly different photochemistry is not unexpected.

Most exciting was the unusual and new arrangement exhibited by 1,1,2,2-tetramethyl-3-(2,2-diphenylvinyl)-cyclopropane (**7**). The reaction may be depicted as proceeding by three-ring fission due to conjugation of the excited diphenylvinyl group with the adjacent three-ring bond. Actually, one would expect the excitation to include this bond. Fission leads to biradical **19** which[28] then undergoes a unique methyl migration (eq 7). Independent of whether this species is a singlet or a triplet,[28] the molecule during the rearrangement process itself (step 3, eq 7) must be a singlet, since product having only paired electrons is developing.

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(23) For this consideration, one need not consider the signs given in Figure 1 as relevant. The orbitals given are merely a basis set and the plus–minus orientation is arbitrary and could have been taken with no unlike sign overlap. Only in cyclic arrays does one find cases of enforced plus–minus overlap in the basis set (as in Möbius systems[24]).

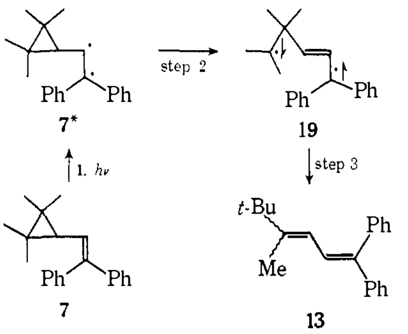
(24) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564, 1566 (1966).

(25) Interestingly, this predicts possible enhancement of the reaction rate with phenyl substitution at carbon-3.

(26) We note that the ultraviolet spectra of 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene (**5**) and 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**17**) give no evidence of vinyl–vinyl interaction. The spectra are very similar to one another and to that of diphenylethylene, suggesting no appreciable ground-state interaction or interaction during a vertical excitation process.

(27) The decay rates referred to here include not only direct decay of the excited state **5*** but also decay to reactant ground state by all species along the reaction coordinate prior to the rate-limiting stage of the reaction.

(28) To the extent that the two odd electron moieties are well separated and in a conformation with little overlap, the singlet–triplet question is not meaningful since the species will be a double doublet. As interaction between the halves diminishes, the singlet–triplet energy difference will diminish and the rate of electron relaxation allowing singlet–triplet interconversion is expected to become increasingly rapid.



(7)

Experimental Section[29]

2,2-Dimethyl-4,4-diphenyl-3-butenal. The synthesis of this aldehyde closely followed, except for modification of two steps, the five-step sequence previously described by Julia and Baillarge.[7]

2-Methyl-3-phenoxypropene was prepared[7] in 76% yield from phenol and 3-chloro-2-methylpropene: nmr (CCl_4) τ 3.00 (m, 5 H, arom), 4.98 (m, 1 H, vinyl), 5.10 (m, 1 H, vinyl), 5.70 (broad s, 2 H, OCH_2), and 8.22 (broad s, 3 H, allylic CH_3).

A solution of 241 g (1.63 mol) of 2-methyl-3-phenoxypropene in 350 ml of dimethyl sulfoxide, to which had been added 50 g (0.45 mol) of commercial potassium *t*-butoxide, was heated to 100° under nitrogen and this temperature was maintained for 20 min. The dark solution was cooled to room temperature and 2 l. of water was then added slowly. The mixture was extracted with ether and the extract washed thoroughly with water and dried. Removal of the ether yielded a dark red oil which was distilled under reduced pressure to give pure 2-methyl-3-phenoxy-2-propene: bp 115° (15 mm); nmr (CCl_4) τ 2.98 (m, 5 H, arom), 3.87 (m, 1 H, vinyl), 8.32 (d, J = 1.0 cps, 3 H, allylic CH_3), and 8.38 (d, J = 1.2 cps, 3 H, allylic CH_3).

Treatment of 2-methyl-3-phenoxy-2-propene with ethyl diazoacetate in the presence of copper bronze under the conditions of Julia and Baillarge[7] followed by reaction of the resulting ester (purified by distillation only) with excess phenyllithium in ether gave diphenyl(2,2-dimethyl-3-phenoxycyclopropane)methanol: mp 99° (lit.[7] 101°); nmr (CCl_4) τ 2.80 (m, 15 H, arom), 6.10 (s, 1 H, OH, removed by shaking with deuterium oxide), 6.35 (d, J = 7 cps, 1 H, OCH), 8.45 (d, J = 7 cps, 1 H, Ph_2CCH). 8.80 (s, 3 H, CH_3), and 8.92 (s, 3 H, CH_3).

A solution of 20.0 g (0.058 mol) of diphenyl(2,2-dimethyl-3-phenoxycyclopropane)methanol in 150 ml of acetone was added to a solution of 10.0 g of potassium bisulfate[30] in 100 ml of water and the heterogeneous mixture was refluxed for 5.5 hr and then cooled and concentrated to approximately 120 ml. The product was extracted with ether and the extract washed with 5% sodium hydroxide solution and dried. Removal of the solvent gave an oil which was distilled under reduced pressure to yield 11.6 g (80%) of 2,2-dimethyl-4,4-diphenyl-3-butenal:[7] bp 135° (0.20 mm); nmr (CCl_4) τ 0.9 (s, 1 H, aldehydic H), 2.88 (m, 10 H, arom), 4.03 (s, 1 H, vinyl), and 8.93 (s, 6 H, methyls).

1,1-Diphenyl-3,3,5-trimethyl-1,4-hexadiene. A mixture of 13.2 g (30.5 mmol) of finely powered isopropyltriphenylphosphonium iodide[31] was stirred in 150 ml of hexane under nitrogen at room temperature and 11 ml of 2.4 *M* *n*-butyllithium in hexane (26.4 mmol) was added. The mixture was then refluxed under nitrogen for 2 hr. At the end of this time butane was no longer being evolved. The red solution of the ylide was cooled to room temperature and a solution of 6.25 g (25 mmol) of 2,2-dimethyl-4,4-diphenyl-3-butenal in 25 ml of ether was added. The mixture was refluxed for 1 hr and stirred overnight at room temperature. The precipitated triphenylphosphine oxide was filtered off and washed with hexane. The combined washings and filtrate were concentrated to about 50 ml and this solution was then applied to an alumina column (4 × 20 cm; Fisher alumina, 80–200 mesh) which had been slurry packed in hexane. Elution was with 5% ether in hexane and 500-ml fractions were collected. Fractions 1 and 2 each contained a colorless oil and were united. Fraction 3 and later fractions were empty. Distillation of the oil under reduced pressure gave 4.85 g (70%) of 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene, bp 131° (0.2 mm). Spectral properties were: ir (CS_2) 3.23, 3.26, 3.30, 3.37, 3.41, 3.49, 6.27, 7.29, 7.38, 8.93, 9.33, 9.70, 10.22, 11.50, 12.26, 13.24, 13.82, 14.30, and 15.60 μ; nmr (CCl_4) τ 2.87 (m, 10 H, arom), 3.83 (s, 1 H, vinyl H), 5.00 (m, 1 H, vinyl H), 8.34 (d, J = 1.5 cps, 3 H, allylic methyl), 8.53 (d, J = 1.7 cps, 3 H, allylic methyl), and 8.90 (s, 6 H, methyls); uv $\lambda_{max}^{95\%\ EtOH}$ 249 mμ (ϵ 13,160).

Anal. Calcd for $C_{21}H_{24}$: C, 91.30; H, 8.70. Found: C, 91.21; H, 8.82.

Direct Photolysis of 1,1-Diphenyl-3,3,5-trimethyl-1,4-hexadiene. A solution of 2.00 g (7.25 mmol) of 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene in 200 ml of *t*-butyl alcohol was purged with purified nitrogen[32] for 45 min before and during photolysis. The irradiation was carried out for 3 hr using a 450-W Hanovia medium-pressure mercury lamp with Corex glass filter, all in a water-cooled immersion well. Solvent removal *in vacuo* gave 2.03 g of pale yellow oil. Recrystallization from methanol provided 830 mg of 1,1-dimethyl-2,2-diphenyl-3-(2-methylpropenyl)cyclopropane, mp 77°. Spectral properties were: ir (CS_2) 3.23, 3.26, 3.29, 3.36, 3.39, 3.42, 3.47, 3.65, 6.27, 7.28, 8.68, 8.97, 9.27, 9.76, 10.61, 11.90, 13.02, 13.52, 14.20, 14.40, and 15.72 μ; nmr (CCl_4) τ 2.85 (m, 10 H arom), 5.27 (d of m's, J_d = 9 cps, 1 H, vinyl), 7.93 (d, J = 9 cps, 1 H, methine), 8.14 (d, J = 1.2 cps, 3 H, allylic CH_3), 8.28 (d, J = 1.0 cps, 3 H, allylic CH_3), 8.88 (s, 3 H, cyclopropyl CH_3), and 8.97 (s, 3 H, cyclopropyl CH_3); uv $\lambda_{max}^{95\%\ EtOH}$ 225 mμ (ϵ 7310).

Anal. Calcd for $C_{21}H_{24}$: C, 91.30; H, 8.70. Found: C, 90.92; H, 8.88.

The mother liquors from the above crystallization were concentrated and the resulting oil (1.19 g) was chromatographed on a silicic acid column (Mallinckrodt Silicar-CC7; 2 × 90 cm) which had been slurry packed in hexane. Elution was with 5 l. of hexane, 500 ml of 5% ether in hexane, and then 3 l. of 10% ether in hexane. The eluent was scanned at 230 mμ and 40-ml fractions were collected.

Two peaks were observed in the scan: fractions 1–53, empty; 54–116, 549 mg of unchanged 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene; 117–130, empty; 131–176, 696 mg of an oil which crystallized on standing and proved to be pure 1,1-dimethyl-2,2-diphenyl-3-(2-methylpropenyl)cyclopropane, mp 76°.

Characterization of 1,1-Dimethyl-2,2-diphenyl-3-(2-methylpropenyl)cyclopropane. Degradation to 2,2-Dimethyl-3,3-diphenylcyclopropanecarboxylic Acid. The method used was based on that described by von Rudloff.[8] A solution containing 1.05 g of sodium meta-periodate, 30 mg of potassium permanganate, and 50 mg of potassium carbonate in 50 ml of water was added to a solution of 100 mg (0.362 mmol) of 1,1-dimethyl-2,2-diphenyl-3-(2-methylpropenyl)cyclopropane in 50 ml of dioxane. The mixture was stirred at room temperature for 1 hr and 1 g of potassium hydroxide was then added and allowed to dissolve. The mixture was washed thoroughly with ether and then acidified with concentrated hydrochloric acid. The liberated acidic material was extracted with ether and the extract washed with water and dried. Removal of the ether gave a brown oil which deposited crystals on addition of hexane. These were filtered off to give 49 mg (50%) of a yellow solid, mp 200–220°. Recrystallization from benzene–hexane gave 35 mg, mp 223–227°. The ir and nmr spectra of this solid were identical with those of authentic 2,2-dimethyl-3,3-diphenylcyclopropanecarboxylic acid.[2] A melting point determined on a mixture of the acids from the two sources showed no depression.

2,3-Dimethyl-2-butene. This olefin was prepared by a method similar to that described by Applequist and Babad.[33] Reaction of methylmagnesium iodide with ethyl isobutyrate yielded 2,3-dimethyl-2-butanol, bp 68° (105 mm), which was dehydrated by refluxing with *p*-toluenesulfonic acid in toluene. Distillation of the material boiling over the range 50–80° through a spinning band column gave two fractions: fraction 1, bp 52°, 21%, was seen from its nmr spectrum to be 2,3-dimethylbutene [τ (CCl_4) 5.34 (m, 2 H, vinyl), 7.80 (m, 1 H, methine H), 8.38 (s, 3 H, allylic CH_3), and 8.98 (d, J = 5 cps, 6 H, isopropyl methyls)]; fraction 2, bp 72°, 61%, was the required 2,3-dimethyl-2-butene [τ (CCl_4) 8.35 (s)].

2,2,3,3-Tetramethylcyclopropanecarboxylic Acid. The method used was based on that of Meschcheryakov and Dolgii.[9] A mixture of 60.1 g (526 mmol) of ethyl diazoacetate and 15.0 g (179 mmol) of 2,3-dimethyl-2-butene was added dropwise with vigorous stirring over 3 hr to a suspension of 7.5 g of copper bronze (Leo Uhlfelder

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[29] All melting points were taken on a hot-stage apparatus which had been calibrated with known compounds.

[30] This modification is due to Dr. A. A. Baum and greatly simplified purification of the product aldehyde.

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

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

[33] D. E. Applequist and H. Babad, *J. Org. Chem.*, **27**, 288 (1962).

Co.) in 45.0 g of 2,3-dimethyl-2-butene heated in a bath at 75°. When the addition had been completed the temperature was maintained at 75° for a further 1 hr. The mixture was cooled and the copper filtered off. The filtrate was distilled under reduced pressure yielding 37.6 g (42% based on the ethyl diazoacetate used) of ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate, bp 76–78° (15 mm) [lit.[9] 76–77° (15 mm)].

A solution of 15.2 g (80.94 mmol) of ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate in 100 ml of methanol containing 15.1 g (267.3 mmol) of potassium hydroxide was refluxed for 3 hr. The solvent was removed on the rotary evaporator, water was added, and the mixture was washed with ether. The aqueous alkaline phase was acidified with hydrochloric acid and extracted with ether. The extract was washed with water and dried. Removal of the ether gave 11.31 g (89%) of crude acid. Recrystallization from benzene gave 2,2,3,3-tetramethylcyclopropanecarboxylic acid, mp 119° (lit.[9] 121°).

Methyl 2,2,3,3-Tetramethylcyclopropylacetate. A mixture of 21.0 g (147.9 mmol) of 2,2,3,3-tetramethylcyclopropanecarboxylic acid and 40 ml of thionyl chloride was refluxed for 1 hr. The excess thionyl chloride was removed at 30° *in vacuo*. The acid chloride was dissolved in 200 ml of dry ether and added dropwise to diazomethane (450 mmol) in 600 ml of ether at 0–5°. The mixture was stirred at this temperature for 1 hr and the ether and excess diazomethane were removed in a stream of nitrogen. The resulting oily diazo ketone was dissolved in 200 ml of warm (40°) purified dioxane[34] and added slowly to a vigorously stirred suspension of freshly prepared silver oxide in 200 ml of water containing 100 ml of dioxane, 20 g of sodium thiosulfate pentahydrate, and 25 g of sodium carbonate at 70°. When the addition had been completed, the temperature was raised to reflux point, a further 5.6 g of silver oxide was added, and the mixture was refluxed with vigorous stirring for 4 hr, then cooled to room temperature and filtered. The filtrate was further basified by addition of 10 g of sodium hydroxide pellets, 200 ml of water was added, and the solution was washed thoroughly with ether. The mixture was acidified with concentrated hydrochloric acid and then extracted with ether. The extract was washed thoroughly with water and dried. Concentration yielded 8.9 g of acidic material which was added in 100 ml of ether to diazomethane (200 mmol) in 200 ml of ether. Removal of the excess diazomethane and ether *in vacuo* gave a yellow oil which was distilled under reduced pressure to give 8.2 g (33%) of methyl 2,2,3,3-tetramethylcyclopropylacetate: bp 60° (3.7 mm); nmr (CCl_4) τ 6.40 (s, 3 H, ester CH_3), 7.82 (d, J = 7.5 cps, 2 H, CH_2), 8.92 (s, 6 H, cyclopropyl methyls), 9.08 (s, 6 H, cyclopropyl methyls), and 9.50 (t, J = 7.5 cps, 1 H, cyclopropyl H).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.59; H, 10.59. Found: C, 70.57; H, 10.58.

1,1-Diphenyl-2-(2,2,3,3-tetramethylcyclopropane)ethanol. Phenyllithium in ether was prepared from 9.1 g (58 mmol) of bromobenzene in 15 ml of ether and 1.0 g of lithium in 50 ml of ether. A solution of 2.14 g (12.6 mmol) of methyl 2,2,3,3-tetramethylcyclopropylacetate in 15 ml of ether was added dropwise to the phenyllithium solution with stirring under nitrogen at room temperature. The solution was then refluxed for 30 min and cooled, and water was carefully added. The mixture was extracted with ether and the extract washed with water and dried. Removal of the ether gave a yellow oil which was crystallized from hexane to give 2.68 g (72%) of 1,1-diphenyl-2-(2,2,3,3-tetramethylcyclopropane)ethanol: mp 112°; nmr (CCl_4) τ 2.87 (m, 10 H, arom), 7.20 (s, 1 H, OH, removed by shaking with deuterium oxide), 7.92 (d, J = 6 cps, 2 H, CH_2), 9.10 (s, 6 H, cyclopropyl CH_3), 9.26 (s, 6 H, cyclopropyl CH_3), and 9.77 (t, J = 6 cps, 1 H, cyclopropyl H).

Anal. Calcd for $C_{21}H_{26}O$: C, 85.74; H, 8.84. Found: C, 85.87; H, 8.88.

1,1,2,2-Tetramethyl-3-(2,2-diphenylvinyl)cyclopropane. A homogeneous mixture of 4.00 g (13.5 mmol) of 1,1-diphenyl-2-(2,2,3,3-tetramethylcyclopropane)ethanol and 8.00 g of alumina (Woelm, activity grade 1) was heated at 180° for 30 min. After cooling to room temperature the residue was ether extracted. The extract was filtered and concentrated to yield an oil which crystallized from methanol to give 2.16 g (57%) of 1,1,2,2-tetramethyl-3-(2,2-diphenylvinyl)cyclopropane, mp 84°. Spectral properties were: ir (Nujol mull): 6.20, 6.27, 6.36, 7.69, 8.48, 8.95, 9.33, 9.75, 10.00, 10.20, 10.30, 10.40, 10.71, 10.92, 11.12, 11.35, 12.52, 13.17, 13.71, 14.40, 15.55, and 16.00 μ; uv $\lambda_{max}^{95\%\ EtOH}$ 269 (ϵ 16,630) and 222 mμ (ϵ 14,690); nmr (CCl_4) τ 2.83 (m, 10 H, arom), 4.25 (d, J = 9 cps, 1 H, vinyl H), 8.88 (s, 6 H, cyclopropyl CH_3), 8.96 (s, 6 H, cyclopropyl CH_3), and 9.05 (d, J = 9 cps, 1 H, cyclopropyl H).

Anal. Calcd for $C_{21}H_{24}$: C, 91.30; H, 8.70. Found: C, 91.26; H, 8.88.

Quantum Yield Apparatus and Equipment. The light from a GE AH6 high-pressure mercury arc centered at the focus of a parabolic aluminum reflector 13.7 cm long and 14.0 cm in diameter was filtered by a three-compartment water-cooled cell. The compartments were separated by gasketed quartz disks, 2.4 cm thick and 12 cm in diameter.

The photolysis cell contained two identical compartments, each 12 cm in diameter with a 5-cm optical path. Aliphatic epoxy (uv transparent and nonfluorescent) cement was used for sealing the quartz faces. The cells were fitted with a heat exchanger coil, a thermistor probe inlet, nitrogen inlet, and a Trubore stirrer. The light output was monitored with an RCA 935 phototube mounted between the filter and irradiation cells. All irradiations were carried out at 27.0 ± 0.2°. Before irradiation, vanadous-purified nitrogen[32] was bubbled through the solution for 0.5 hr, and during the irradiation a positive pressure of nitrogen was maintained over the solution.

Actinometry. Each determination required three runs: (1) irradiation with both cells containing actinometer; (2) irradiation with the first cell containing photolysis solution and the second cell containing actinometer; and (3) irradiation with both cells containing actinometer. Potassium ferrioxalate actinometry[35] was employed, and a quantum yield of 1.23[35] was assumed.

Filter Solutions. Transmission curves for the filter solutions were measured using a three-compartment cell with quartz end and separating plates, each compartment being 2.4 cm long. A 7.2-cm water reference cell was used. Transmission curves were determined just prior to and following each run.

Filter A. Cell I, 2 *M* nickel sulfate hexahydrate in 5% sulfuric acid; II, 5% sulfuric acid saturated with cobalt sulfate heptahydrate at 25° and diluted with 25% of its volume of 5% sulfuric acid; cell III, 2 × 10^{-4} *M* bismuth trichloride in 10% hydrochloric acid; transmission (250–305 mμ, maximum at 273 mμ): 220–250, 0%; 260, 11%; 270, 28%; 280, 27%; 290, 14%; 300, 2%; 305–400 mμ, 0%.

Filter B. Cell I, 225 g of nickel sulfate hexahydrate in 500 ml of 10% sulfuric acid; cell II, 140 g of cobalt sulfate heptahydrate in 500 ml of 10% sulfuric acid; cell III, 1.75 g of stannous chloride dihydrate in 500 ml of 10% hydrochloric acid; transmission (295–355 mμ, maximum at 318 mμ): 220–295, 0%; 300, 2%; 310, 20%; 320, 29%; 330, 18%; 340, 5%; 350, 1%; 355–450 mμ, 0%.

Solvent and Sensitizer. Benzophenone (Eastman) was recrystallized from 95% ethanol, mp 49–50°. *t*-Butyl alcohol was distilled from calcium hydride.

Direct Quantum Yields. 1,1-Diphenyl-3,3,5-trimethyl-1,4-hexadiene was irradiated in dilute *t*-butyl alcohol solution through filter A to about 20% conversion. All runs were made in 725 ml of solvent. The solvent was removed *in vacuo* below 40°. The product was chromatographed on a 2.5 × 90 cm column of Mallinckrodt Silicar-CC7 which had been slurry packed in hexane. Elution was with hexane, the eluent was scanned at 230 mμ, and 40-ml fractions were collected. The diene and product vinylcyclopropane were cleanly separated under these conditions and the quantum yields were based on the amounts of isolated vinylcyclopropane. Data for individual quantum yields are listed as follows: weight of diene, amount of light, weight of recovered materials, and quantum yields.

Run 1. Starting diene (500.1 mg, 1.81 mmol); 3.85 mEinsteins; recovered diene (387.2 mg, 1.40 mmol); photovinylcyclopropane (108.9 mg, 0.38 mmol); ϕ = 0.102 ± 0.007.

Run 2. Starting diene (623.2 mg, 2.26 mmol); 4.12 mEinsteins; recovered diene (513.3 mg, 1.86 mmol); photovinylcyclopropane (104.9 mg, 0.38 mmol); ϕ = 0.093 ± 0.007.

Sensitized Quantum Yields. 1,1-Diphenyl-3,3,5-trimethyl-1,4-hexadiene and benzophenone were dissolved in 725 ml of *t*-butyl alcohol and irradiated through filter **B**. The solvent was removed *in vacuo* below 40°. The product was chromatographed on a 2.5 × 90 cm column of Mallinckrodt Silicar-CC7 which had been slurry-packed in hexane. Elution was with hexane, the eluent was scanned at 230 mμ, and 40-ml fractions were collected. Quantum yields were based on the amount of isolated vinylcyclopropane. Data for

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(34) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 333.

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

individual quantum yield runs are listed as follows: weight of diene, weight of benzophenone, amount of light, weight of recovered materials, and quantum yields.

Run 3. Starting diene (976.5 mg, 3.54 mmol); benzophenone (10.00 g, 54.9 mmol); 11.92 mEinsteins; recovered diene (933.1 mg, 3.38 mmol); photovinylcyclopropane (28.2 mg, 0.10 mmol); $\phi = 0.008 \pm 0.002$.

Run 4. Starting diene (929.3 mg, 3.37 mmol); benzophenone (10.11 g, 55.5 mmol); 20.47 mEinsteins; recovered diene (858 mg, 3.11 mmol); photovinylcyclopropane (44 1 mg, 0.16 mmol); $\phi = 0.008 \pm 0.002$.

Comparison of the ultraviolet spectra of the diene with that of benzophenone (both in *t*-butyl alcohol as solvent) indicated that in the benzophenone sensitized runs more than 98% of the light was being absorbed by the benzophenone using filter B.

Test for Energy Transfer to Diene by Benzophenone. Photoreduction of Benzophenone by Benzhydrol. A solution of 6.000 g (33.00 mmol) of benzophenone and 2.000 g (10.9 mmol) of benzhydrol in 230 ml of *t*-butyl alcohol was purged with purified nitrogen[32] for 1 hr before and during the photolysis. Irradiation was carried out for 22 min using the Hanovia apparatus with a Pyrex glass filter. Concentration *in vacuo* gave a crystallizing oil (8.073 g) which was subjected to chromatography on a 4 × 90 cm silica gel column (Davison, grade 950) which had been slurry packed in hexane. Elution was with 1.0 l. of 50% benzene in hexane, 1.0 l. of 75% benzene in hexane, 1.0 l. of 90% benzene in hexane, 4.0 l. of benzene, 1.0 l. of 30% ether in benzene, and 1.0 l. of 70% ether in benzene, and 500-ml fractions were collected. Fractions 6–7 gave 1.209 g of a solid, mp 191–194°, characterized as benzpinacol; 8 gave 2.783 g of an oil which on recrystallization from hexane gave 0.818 g of benzpinacol, the mother liquors yielding only benzophenone; 9–17 gave 3.002 g of benzophenone; 18–21 gave 1.312 g of a solid, mp 60–64°, identified as benzhydrol.

Photoreduction of Benzophenone by Benzhydrol with Added 1,1-Diphenyl-3,3,5-trimethyl-1,4-hexadiene. Irradiation of a solution of 6.000 g (33.00 mmol) of benzophenone, 2.000 g (10.9 mmol) of benzhydrol, and 0.504 g (1.83 mmol) of 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene employing the same conditions described for the photoreduction without added diene gave, after concentration *in vacuo*, 8.763 g of an oil which was chromatographed on a 4.0 × 90 cm silica gel column which had been slurry packed in hexane. Elution was with 2.0 l. of 50% benzene in hexane, 3.0 l. of 75% benzene in hexane, 3.5 l. of 85% benzene in benzene, 1.5 l. of 5% ether in benzene, and 2.0 l. of 20% ether in benzene, and 500-ml fractions were collected. Fractions 1–7 gave 0.493 g of an oil which was shown to be unchanged 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene; 13–16 gave 0.132 g of a solid, mp 189–192°, identified as benzpinacol; 17–24 gave 5.930 g of benzophenone; 25–27 gave 2.181 g of a crystallizing oil which was recrystallized from hexane to give 1.512 g of benzhydrol, the mother liquors being shown to consist of a mixture of benzhydrol and benzophenone.

Photolysis of 1,1,2,2-Tetramethyl-3-(2,2-diphenylvinyl)cyclopropane. A solution of 1.00 g (3.63 mmol) of 1,1,2,2-tetramethyl-3-(2,2-diphenylvinyl)cyclopropane in 120 ml of *t*-butyl alcohol was purged with purified nitrogen[32] for 1 hr before and during photolysis. The irradiation was carried out for 1.5 hr in the Hanovia apparatus using a Vycor glass filter. Removal of the solvent *in vacuo* gave a pale yellow oil, 996 mg, which was chromatographed on a silicic acid column (Mallinckrodt Silicar-CC7; 8 × 96 cm) which had been slurry packed in hexane. Elution was with hexane. The eluent was scanned at 270 mμ and 40-ml fractions were collected: fractions 1–356, empty; 357–439, 258 mg of unchanged 1,1,2,2-tetramethyl-3-(2,2-diphenylvinyl)cyclopropane, mp 82°; 440–479, 178 mg of a mixture of 1,1,2,2-tetramethyl-3-(2,2-diphenylvinyl)cyclopropane and 1,1-diphenyl-4,5,5-trimethyl-1,3-hexadiene; 480–660, 496 mg of impure 1,1-diphenyl-4,5,5-trimethyl-1,3-hexadiene. Recrystallization of fractions 480–660 from ethanol gave 324 mg of pure 1,1-diphenyl-4,5,5-trimethyl-1,3-hexadiene, mp 67°. The nmr spectrum of the mother liquors showed them to be predominantly 1,1-diphenyl-4,5,5-trimethyl-1,3-hexadiene containing some impurities. The spectral properties of the diene were identical with those reported for authentic 1,1-diphenyl-4,5,5-trimethyl-1,3-hexadiene (*vide infra*) and a mixture melting point with authentic material showed no depression.

1,1-Diphenylpropene. This hydrocarbon was prepared by sulfuric acid dehydration[36] of 1,1-diphenylpropanol, obtained by reaction of ethyl propionate with excess phenyllithium.[36]

3-Bromo-1,1-diphenylpropene. Treatment of 1,1-diphenylpropene with N-bromosuccinimide in carbon tetrachloride[37] gave the required bromide.

Diethyl 3,3-Diphenyl-2-propenylphosphonate. A mixture of 9.0 g (54.2 mmol) of triethyl phosphite and 12.0 g (43.9 mmol) of 3-bromo-1,1-diphenylpropene was heated slowly. At approximately 120° a vigorous reaction set in and ethyl bromide, bp 39°, distilled out of the mixture. The temperature was raised to 150° for 10 hr and the mixture was distilled at reduced pressure to yield 8.13 g (56%) of diethyl 3,3-diphenyl-2-propenylphosphonate, bp 185° (0.3 mm). The oil solidified on standing and on recrystallization from hexane had mp 56°: ir (Nujol mull) 6.11, 6.26, 6.36, 6.70, 7.50, 7.63, 7.80, 7.97, 8.27, 9.30–9.85 (broad), 10.35, 11.01, 11.30, 11.90, 12.29, 12.82, 13.00, 13.90, 14.20, 14.30, and 15.98 μ; nmr (CCl_4) τ 2.80 (m, 10 H, arom), 4.02 (d of t's, $J_{H-H} = 7.5$, $J_{P-H} = 7.5$ cps, 1 H, vinyl), 6.05 (d of q's, $J_{H-H} = 7$ cps, 4 H, ethyl CH_2), 7.47 (d of d's, $J_{H-H} = 7.5$, $J_{P-H} = 22$ cps, 2 H, allylic CH_2), and 8.77 (t, $J = 7$ cps, 6 H, methyls).

Anal. Calcd for $C_{19}H_{23}O_3P$: C, 69.03; H, 6.96; P, 9.47. Found: C, 68.81; H, 6.88; P, 9.65.

1,1-Diphenyl-4,5,5-trimethyl-1,3-hexadiene. A 54% mineral oil suspension of sodium hydride (1.35 g; 30.4 mmol) was washed with hexane and then 30 ml of dry 1,2-dimethoxyethane, 9.11 g (27.6 mmol) of diethyl 3,3-diphenyl-2-propenylphosphonate, and 3.15 g (31.5 mmol) of pinacolone were added. The mixture was heated under reflux for 2.5 hr and the dark solution was then cooled to room temperature. Water was added and the mixture was extracted with ether. The extract was washed with water and dried. Removal of the ether gave a pale yellow oil which was distilled under reduced pressure to give 5.19 g (68%) of 1,1-diphenyl-4,5,5-trimethyl-1,3-hexadiene, bp 155° (1.2 mm). The oil solidified on standing and on recrystallization from ethanol had mp 68°. Spectral properties were: ir (CS_2) 3.23, 3.26, 3.30, 3.37, 3.43, 3.48, 6.17, 6.29, 7.29, 7.37, 8.07, 8.63, 9.17, 9.32, 9.73, 11.33, 12.82, 13.11, 13.48, 14.32, and 15.95 μ; uv $\lambda_{max}^{95\%\ EtOH}$ 299 mμ (ε 24,700) and λ_{sh} 225 mμ (ε 15,135); nmr (CCl_4) τ 2.80 (m, 10 H, arom), 3.22 (d, $J = 11$ cps, 1 H, vinyl H at C-2), 4.00 (d of q's, $J_d = 11$ cps, $J_q = 1.5$ cps, 1 H, vinyl H at C-3), 8.17 (d, $J = 1.5$ cps, 3 H, allylic CH_3), and 9.01 (s, 9 H, *t*-butyl).

Anal. Calcd for $C_{21}H_{24}$: C, 91.30; H, 8.70. Found: C, 91.08; H, 8.79.

Photolysis of 1,1-Dimethyl-2,2-diphenyl-3-(2-methylpropenyl)-cyclopropane. A solution of 500 mg (1.81 mmol) of 1,1-dimethyl-2,2-diphenyl-3-(2-methylpropenyl)cyclopropane in 125 ml of *t*-butyl alcohol was purged with purified nitrogen[32] for 45 min before and then during photolysis. The irradiation was carried out for 2.5 hr in the Hanovia apparatus using a Vycor glass filter. Solvent removal *in vacuo* gave 503 mg of a pale yellow oil. The oil was applied to a preparative thin-layer plate (silica gel) and developed with hexane. Five developments separated the material into three bands. Each band was isolated separately and the adsorbed material recovered by extraction with ether.

The fastest moving band yielded 170 mg of an oil, bp 145° (12 mm); nmr (CCl_4) τ 2.9 (m, 10 H, arom) and 8.20 (s, 6 H, allylic CH_3's). Comparison of the spectra of this photoproduct (ir, uv, nmr) with those of an authentic specimen of 1,1-diphenyl-2-methylpropene[38] confirmed their identity.

The second band yielded 154 mg of an oil which solidified to give unchanged 1,1-dimethyl-2,2-diphenyl-3-(2-methylpropenyl)cyclopropane.

The slowest moving band yielded 165 mg of a yellow oil which solidified at low temperature and on recrystallization from methanol at 0° gave a colorless solid, mp 56°. The spectral properties of this photoproduct suggested that it was benzhydryl *t*-butyl ether and comparison with an authentic sample (ir, uv, nmr, mixture melting point; *vide infra*) confirmed this.

Diphenyldiazomethane. Diphenyldiazomethane was prepared by the method of Miller[39] from benzophenone hydrazone and mercuric oxide.

Benzhydryl *t*-Butyl Ether. Irradiation of Diphenyldiazomethane in *t*-Butyl Alcohol. A solution of 3.00 g (15.46 mmol) of diphenyldiazomethane in 250 ml of *t*-butyl alcohol was irradiated in the Hanovia apparatus through a Pyrex glass filter for 4 hr. The deep

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[36] P. Beltrame, S. Carra, P. Macchi, and M. Simonetta, *J. Chem. Soc.*, 4386 (1964).

[37] K. Ziegler, A. Spath, E. Schaaf, W. Schumann, and E. Winkelmann, *Justus Liebigs Ann. Chem.*, **551** 80 (1942).

[38] J. Levy, *Bull. Soc. Chim. Fr.*, **29**, 878 (1921).

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

purple color of the diphenyldiazomethane had disappeared at the end of this time. Removal of the solvent *in vacuo* yielded 3.38 g (90%) of a pale yellow oil which crystallized from methanol at 0° to give 2.53 g of benzhydryl *t*-butyl ether, mp 57°. Spectral properties were: ir (Nujol mull) 6.27, 7.70, 8.13, 8.45, 9.25, 9.52, 9.81, 11.15, 11.85, 13.04, 13.57, 14.46, and 15.64 μ; uv $\lambda_{\text{sh}}^{95\%\ \text{EtOH}}$ 218 (ϵ 13,920), $\lambda_{\max}$ 248 (ϵ 504), 253 (ϵ 576), 259 (ϵ 610), 265 (ϵ 528), and λ_{sh} 268 mμ (ϵ 370); nmr (CCl_4) τ 2.81 (m, 10 H arom), 4.51 (s, 1 H, OCH), and 8.81 (s, 9 H, *t*-butyl).

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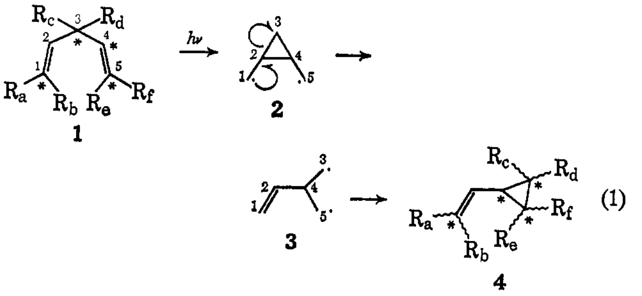
Stereochemical Aspects of the Di-π-methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry. LVII[1]

Howard E. Zimmerman and Albert C. Pratt

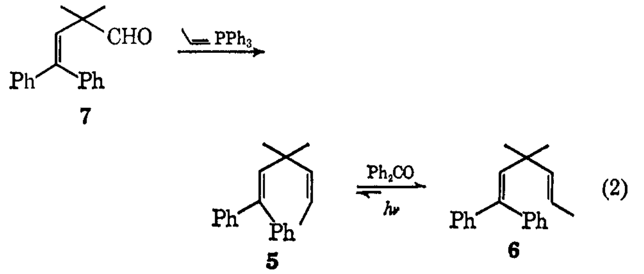
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received January 22, 1970

Abstract: *cis*- and *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (**5** and **6**) were synthesized and configurations assigned. These compounds were found to undergo the di-π-methane rearrangement on irradiation to afford the stereoisomeric 1,1-dimethyl-2,2-diphenyl-3-propenylcyclopropanes (**8** and **9**) whose configurations were established. Although 1,1,2-trimethyl-3-(2,2-diphenylvinyl)cyclopropane (**10**) was an *a priori* product, this was not formed. Thus the direction of the di-π-methane rearrangement was similar to that of the previously studied 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene, and again the electron delocalizing groups (*i.e.*, phenyl) appeared on the three ring rather than the double bond of the product. This permitted tentative generalization. The reaction was shown to utilize S_1 as the reacting excited state for the di-π-methane rearrangement, while T_1 proved to allow interconversion of reactant stereoisomers. The di-π-methane rearrangements studied proved to be stereospecific with *cis* reactant (**5**) leading to *cis* product (**9**) and *trans*-di-π-methane (**6**) affording *trans*-vinylcyclopropane product (**8**).

In our previous paper[1b] describing the effect of unsymmetrical substitution on the direction of the di-π-methane rearrangement, we noted that the separate processes involved in this molecular rearrangement might well be concerted and not discrete steps. One way of testing this aspect was an investigation of the stereochemistry of the rearrangement. Inspection of eq 1 reveals that there is stereochemistry at carbons 1, 3, 4, and 5. The present investigation was focused on the geometry at carbon-1 during the process. For this study the *cis*- and *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadienes (**5** and **6**) were selected.



Synthetic Aspects and Configurational Assignments. The synthesis of *cis*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (**5**) utilized the Wittig reaction of ethylidenetriphenylphosphorane with the known[2] 2,2-dimethyl-4,4-diphenyl-3-butenal (**7**); note eq 2. The preferential formation of the *cis* stereoisomer is in accord with literature[3] reports on the geometric course of the Wittig reaction. The *trans*-isomer **6** was obtained from the benzophenone sensitized isomerization of **5** (note eq 2).



The stereochemistry of the *cis* and *trans* isomers **5** and **6** was most clearly derived from the infrared spectra of the two compounds. The *trans* isomer **6** has a strong absorption band at 10.33 μ (968 cm^{-1}) characteristic[4a] of *trans*-disubstituted olefins and also present in the other *trans* compounds under study. No corresponding absorption was found in the 9.8–12.5 μ (*i.e.*, 800–1020 cm^{-1}) region for the *cis*-isomer **5**. Since it is normally the *cis* isomer which is formed in the Wittig reaction (*vide supra*), this assignment is reasonable.

Results

Exploratory Photochemistry. Irradiation of *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (**6**) afforded one product (**8**) cleanly in a preparatively useful reaction. Most interestingly, too, the recovered unreacted

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(1) (a) For the preliminary communication, note H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **92** 1409 (1970); (b) for paper LVI of the series *cf.* H. E. Zimmerman and A. C. Pratt, *ibid.*, **92** 6259 (1970).

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

(3) W. P. Schneider, *Chem. Commun.*, 786 (1969).

(4) (a) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 25; (b) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, 1959, p 85.