

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  $\mu$ ; uv  $\lambda_{\text{max}}^{0.5\% \text{ EtOH}}$  218 ( $\epsilon$  13,920),  $\lambda_{\text{max}}$  248 ( $\epsilon$  504), 253 ( $\epsilon$  576), 259 ( $\epsilon$  610), 265 ( $\epsilon$  528),

and  $\lambda_{\text{sh}}$  268  $m\mu$  ( $\epsilon$  370); nmr (CCl<sub>4</sub>)  $\tau$  2.81 (m, 10 H arom), 4.51 (s, 1 H, OCH), and 8.81 (s, 9 H, *t*-butyl).

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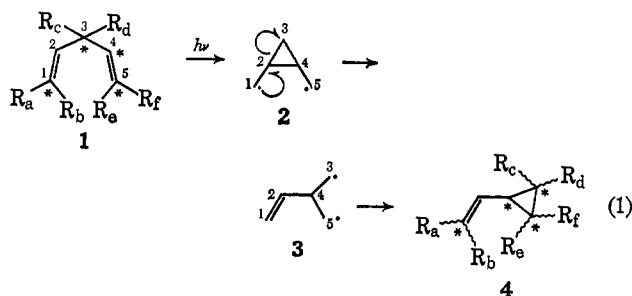
## Stereochemical Aspects of the Di- $\pi$ -methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry. LVII<sup>1</sup>

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**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- $\pi$ -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- $\pi$ -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<sub>1</sub> as the reacting excited state for the di- $\pi$ -methane rearrangement, while T<sub>1</sub> proved to allow interconversion of reactant stereoisomers. The di- $\pi$ -methane rearrangements studied proved to be stereospecific with *cis* reactant (**5**) leading to *cis* product (**9**) and *trans*-di- $\pi$ -methane (**6**) affording *trans*-vinylcyclopropane product (**8**).

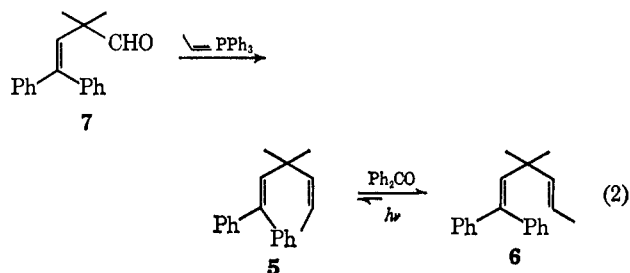
In our previous paper<sup>1b</sup> describing the effect of unsymmetrical substitution on the direction of the di- $\pi$ -methane rearrangement, we noted that the separate processes involved in this molecular rearrangement might well be concerted and not discrete steps. One way of testing this aspect 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 ethylenetriphenylphosphorane with the known<sup>2</sup> 2,2-dimethyl-4,4-diphenyl-3-butenal (**7**); note eq 2. The preferential formation of the *cis* stereoisomer is in accord with literature<sup>3</sup> 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  $\mu$  (968  $\text{cm}^{-1}$ ) characteristic<sup>4a</sup> 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  $\mu$  (*i.e.*, 800–1020  $\text{cm}^{-1}$ ) 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

(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.

Table I. 100 Mcps Nmr and Spin Decoupling of *cis*- and *trans*-1,1-Dimethyl-2,2-diphenyl-3-propenylcyclopropane

Signal position, $\tau$	Description and assignment	Coupling constant, cps	Proton irradiated <sup>b</sup>	Decoupling result	Residual coupling constant, cps <sup>c,d</sup>
<i>trans</i> -1,1-Dimethyl-2,2-diphenyl-3-propenylcyclopropane <sup>a</sup>					
2.89	Multiplet; aromatic				
4.35	Doublet of quartets Vinyl at C-2 of side chain	$J_{\text{CH}_3-\text{H}_2} = 6.5$ $J_{\text{H}_1-\text{H}_2} = 15$	(A) allylic CH <sub>3</sub> (B) H-1	Incomplete <sup>e</sup> Incomplete <sup>f</sup>	
5.08	Doublet of doublet of quartets Vinyl C-1 of side chain	$J_{\text{H}_2-\text{H}_1} = 15$ $H_{\text{cyH}-\text{H}_1} = 10$ $J_{\text{CH}_3-\text{H}_1} = 2$	(A) H-2 (B) cyH (C) Allylic CH <sub>3</sub>	Incomplete <sup>f</sup> Doublet of quartets Doublet of quartets	$J_{\text{H}_2-\text{H}_1} = 15$ $J_{\text{CH}_3-\text{H}_1} = 2$ $J_{\text{H}_2-\text{H}_1} = 15$ $J_{\text{cyH}-\text{H}_1} = 10$
8.02	Doublet; cyH <sup>g</sup>	$J_{\text{cyH}-\text{H}_1} = 10$	H-1	Incomplete <sup>f</sup>	
8.31	Doublet of doublets Allylic CH <sub>3</sub>	$J_{\text{CH}_3-\text{H}_1} = 6.5$ $J_{\text{CH}_3-\text{H}_2} = 2$	(A) H-2 (B) H-1	Incomplete <sup>f</sup> Doublet	$J = 6.5$
8.88	Singlet; cyclopropyl CH <sub>3</sub>				
9.02	Singlet; cyclopropyl CH <sub>3</sub>				
<i>cis</i> -1,1-Dimethyl-2,2-diphenyl-3-propenylcyclopropane <sup>a</sup>					
2.88	Multiplet; aromatic				
4.47	Doublet of quartets Vinyl at C-2 of side chain	$J_{\text{H}_2-\text{CH}_3} = 6$ $J_{\text{H}_1-\text{H}_2} = 11$	(A) Allylic CH <sub>3</sub> (B) H-1	Incomplete <sup>f</sup> Incomplete <sup>f</sup>	
5.07	Doublet of doublet of quartets Vinyl at C-1 of side chain	$J_{\text{H}_2-\text{H}_1} = 11$ $J_{\text{cyH}-\text{H}_1} = 10$ $J_{\text{CH}_3-\text{H}_1} = 2$	(A) H-2 (B) CyH H-1	Incomplete <sup>f</sup> Doublet of quartets Incomplete <sup>f</sup>	$J_{\text{CH}_3-\text{H}_1} = 2$ $J_{\text{H}_2-\text{H}_1} = 11$
7.80	Doublet; cyH	$J_{\text{cyH}-\text{H}_1} = 10$	H-1	Incomplete <sup>f</sup>	
8.14	Doublet of doublets Allylic CH <sub>3</sub>	$J_{\text{H}_1-\text{CH}_3} = 2$ $J_{\text{H}_2-\text{CH}_3} = 6$	(A) H-2 (B) H-1	Incomplete <sup>f</sup> Doublet	$J_{\text{H}_2-\text{CH}_3} = 6$
8.90	Singlet; cyclopropyl CH <sub>3</sub>				
8.98	Singlet; cyclopropyl CH <sub>3</sub>				

<sup>a</sup> Run in carbon tetrachloride with TMS as internal standard. <sup>b</sup> Proton irradiated that affects proton in column 1. <sup>c</sup> Result of proton irradiation in spin decoupling. <sup>d</sup> Coupling constant of the residual peak originally described in columns 1, 2, and 3. <sup>e</sup> Incomplete decoupling but approximated to a doublet of doublets ( $J_{\text{H}_1-\text{H}_2} = 15$  and  $J_{\text{allylic}-\text{H}-\text{H}_2} = 1$ ). <sup>f</sup> Incomplete decoupling. <sup>g</sup> cyH refers to cyclopropyl hydrogen, labeling is  $-\text{CH}=\text{CH}-\text{CH}_3$ .

*trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (**6**) had isomerized only to the extent of *ca.* 2%. Irradiation of *cis*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (**5**) gave only one product (**9**), different from **8**, in low conversion (*e.g.*, 10%) runs and *ca.* 3% isomerization of the unreacted diene **5**. In higher conversion runs, *cis-trans* double bond isomerization of reactant occurred appreciably and led to observation of both photoproducts **8** and **9**.

The structure of the photoproduct obtained from irradiation of *trans*-diene **6** was definitively established by its nmr and infrared spectra as *trans*-1,1-dimethyl-2,2-diphenyl-3-propenylcyclopropane (**8**). The nmr spectrum along with decoupling results are summarized in Table I; both the infrared spectra and nmr results are given in greater detail in the Experimental Section. Inspection of Table I reveals the presence of two vinyl hydrogen absorptions, a three-proton doublet (showing further small coupling) ascribed to a methyl group adjacent to the vinyl group, and two separate methyl

singlets; additionally a one-hydrogen methine doublet deriving from a proton coupled to one of the vinyl hydrogens could be discerned. These data are consistent with a structure such as **8** or **9**, *i.e.*, one of the two possible di- $\pi$ -methane rearrangement products (*cf.* Chart I). This evidence is not consistent with the vinylcyclopropane product **10** which would arise from an alternative di- $\pi$ -methane route (*vide infra*); note Chart I. The stereochemistry about the ethylenic double bond was established again by the infrared spectrum which exhibited the usual  $10.4 \mu$  ( $960 \text{ cm}^{-1}$ ) infrared band characteristic (*vide supra*) of 1,2-*trans*-substituted vinyl derivatives.<sup>4a</sup> This assignment was supported by the large (*i.e.*,  $J = 14$  cps) vinyl H-H coupling constant expected<sup>4b</sup> for *trans*-ethylenic hydrogens. Thus the structure and stereochemistry of the photoproduct from *trans*-diene **6** is established as the cyclopropane stereoisomer **8**.

Similarly, the structure of the photoproduct **9** was derived from nmr and infrared evidence. Reference to

Chart I

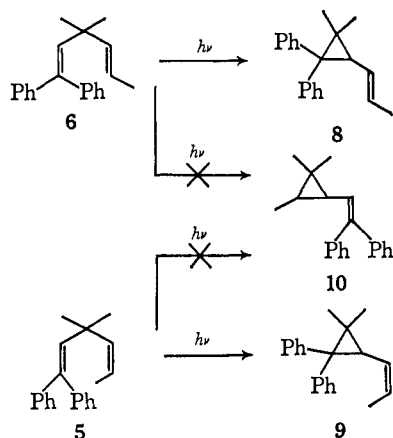


Table I reveals the presence of two isolated methyl groups absorbing as singlets, in addition to an allylic methyl absorption. Also there were again found two vinyl hydrogens and a single cyclopropyl methine. As in the case of the *trans*-stereoisomer **8**, discussed above, the data were inconsistent with the alternative di- $\pi$ -methane product **10**. The nmr, however, was nicely in accord with the assignment of structure **9** to this compound. Additionally, the vinyl-vinyl coupling constant of 10.5 cps for this compound is smaller than that observed for the *trans*-isomer **8** and is in the range expected for a *cis*-1,2-disubstituted alkene.<sup>4b</sup> This assignment of stereochemistry was confirmed by the absence of *trans*-C-H out-of-plane bending absorption in the 10–13  $\mu$  (780–1000  $\text{cm}^{-1}$ ) region.<sup>4a</sup> This infrared difference is the same as noted earlier for the *cis* and *trans* stereoisomers of 1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (**5** and **6**). However, in the diene situation nmr coupling constants were not available (note Experimental Section).

Hence the reaction proved not only to be stereospecific but also to retain the original double bond configuration. Thus *cis*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (**5**) on irradiation afforded *cis*-1,1-dimethyl-2,2-diphenyl-3-propenylcyclopropane (**9**) and *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (**6**) under the same conditions led to *trans*-1,1-dimethyl-2,2-diphenyl-3-propenylcyclopropane (**8**). This reaction course is outlined in Chart I.

**Reaction Multiplicity.** With the idea of determining the behavior of the triplet excited states of the stereoisomeric dienes **5** and **6** and thereby obtaining information on the multiplicity of the di- $\pi$ -methane rearrangement observed in the direct irradiations, *cis*- and *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadienes (**5** and **6**) were individually irradiated in the presence of benzophenone. Under the conditions selected, benzophenone absorbed essentially all of the light and the concentration of diene reactant was adjusted to permit triplet but not singlet energy transfer from the benzophenone.<sup>5</sup>

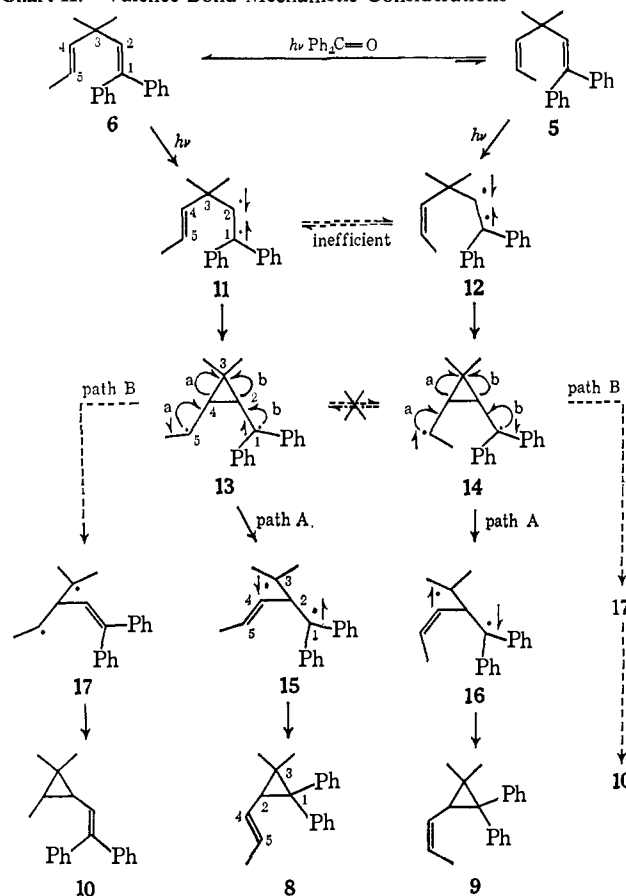
In these experiments it was found that the usual di- $\pi$ -methane rearrangement did not occur and no vinylcyclopropane products were encountered. However, *cis*-*trans* isomerization of the reactant dienes **5** and **6** was observed instead. Thus sensitized irradiation of *cis*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene

(**5**) afforded 97% of *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (**6**). Similarly, sensitized irradiation of the *trans*-isomer **6** under the same conditions gave 3% of *cis*-diene **5**. The total absence of vinylcyclopropane product (**8** and **9**) confirmed the absence of excited state  $T_1$ , as an intermediate in the direct irradiation runs, since the experiments using benzophenone were designed to generate  $T_1$ .

Thus  $T_1$  is not the species responsible for the present di- $\pi$ -methane rearrangement. However, the *cis*-*trans* isomerization may be ascribed to this excited state (*i.e.*,  $T_1$ ). Exclusion of  $T_1$  in the di- $\pi$ -methane rearrangement leaves  $S_1$  and  $T_2$  as candidates. Since in two previous examples<sup>6,7</sup> of the di- $\pi$ -methane rearrangement evidence arguing against  $T_2$  was presented, intervention of  $S_1$  provides the simplest rationale presently.

**Interpretative Discussion.** The first aspect of interest requiring consideration is the selective formation of only one of the two *a priori* possible vinylcyclopropane skeletons. Thus, as depicted in Chart II, no 1,1,2-trimethyl-

Chart II. Valence Bond Mechanistic Considerations



3-(2,2-diphenylvinyl)cyclopropane (**10**) was encountered although this is an alternative di- $\pi$ -methane product differing only in directionality of three-ring opening of species **13** and **14**. A similar directional effect has been observed in our previous study of the photochemistry of 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene.<sup>1</sup> In simplest valence bond terms this selectivity is explicable on the basis of ring opening in **13** (and **14**) by that route which allows maximum electron delocalization throughout. Thus in pathway A the

(5) For considerations involved in such energy transfer experiments, note H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966), footnote 9.

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

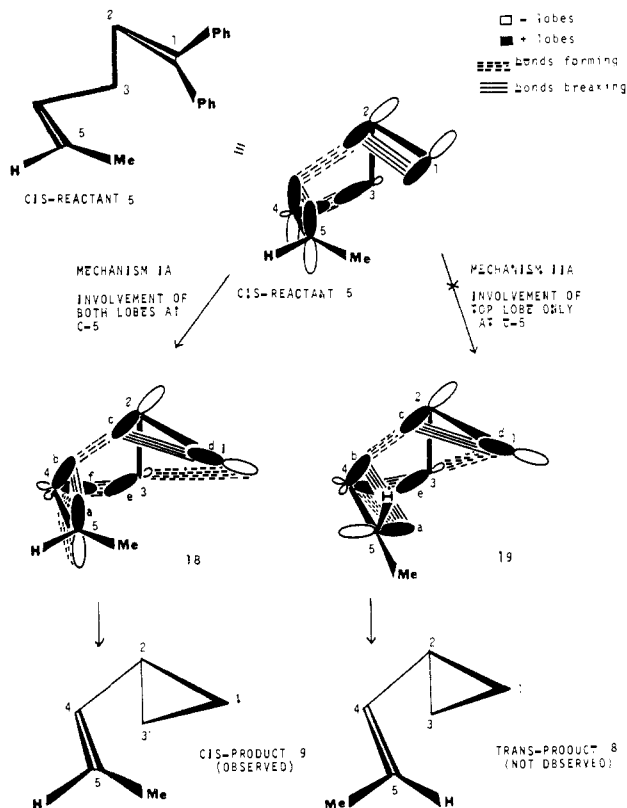
(7) H. E. Zimmerman and G. E. Samuelson, *ibid.*, **91**, 5307 (1969).

odd electron at C-1 remains delocalized by the two phenyl groups at this center while in pathway B this delocalization is lost. Paraphrased and from another viewpoint, there is a lower odd electron density at C-1 than at C-5 in species 13 (or 14) available for participation in three-ring fission.

Previously,<sup>6,7</sup> it has been pointed out that the di- $\pi$ -methane rearrangement may be concerted. This is not inconsistent with the present stepwise formulation of Chart II. Chart II is meant only to depict the individual molecular processes separately for convenience. Thus, while electron delocalization in species 13 and 14 accounts for the reaction directionality, it is certain that these two cannot represent long-lived intermediates. Rotation about bond 4-5 would allow interconversion of 13 and 14 with loss of the observed reaction stereospecificity, in which *cis*-divinylmethane 5 affords *cis*-vinylcyclopropane 9 and *trans*-divinylmethane 6 gives rise to *trans*-vinylcyclopropane 8. Hence 13 and 14, as well as the other biradical-like entities in Chart II, most likely correspond to points on an excited state reaction potential energy surface. Minimally, we can interpret the results as signifying that the rate of rotation in species 13 and 14 must be slow relative to the rate of three-ring opening. However, even here, to the extent that free rotation is impeded by conjugation of the odd electron containing p orbital with the three ring, this just represents initiation of the three-ring opening process and suggests concertedness. With respect to the observed retention of the original propenyl configuration in the reaction, we also note that structures 13 and 15, as well as 14 and 16, are related by least motion.<sup>8</sup>

In Chart III the reaction is depicted in basis orbital terms.<sup>9</sup> This proves useful in understanding the reaction stereochemistry and also bears on the reaction directionality discussed above in terms of discrete valence bond structures. Chart III considers two of a number of different stereochemical possibilities for the 4-5 double bond<sup>10</sup> and uses the *cis*-isomer 5 arbitrarily for illustration. Thus in Chart III there are two orbital arrays, 18 and 19, corresponding to species following the two *a priori* possible stereochemical reaction courses (mechanisms IA and IIA in Chart III). Species 18 is formed by bonding using both lobes of the p orbital at C-5 as the reaction proceeds while 19 arises from utilization of only one such lobe, the one pictured as

Chart III. Stereochemical Course of the Rearrangement. Lack of Pivoting about Bond 4,5 and Möbius Six-Orbital Allowedness Depicted



initially above the 4-5 double bond plane. Thus in the formation of 18 the bottom lobe of the p orbital at C-5 begins to bond with the orbital at C-4 originally involved in  $\sigma$  bonding to C-3. In contrast, the top lobe of the p orbital at C-5 is used for this bonding as 19 is generated; this results from clockwise twisting about the 4-5 bond as 19 is formed from 5. Further molecular change of species 18 can be seen to lead to *cis*-vinylcyclopropane product 9 with the entire pathway requiring little twisting about the 4-5 bond (least motion). Contrariwise, species 19 proceeds onward to *trans*-product 8 with the overall transformation requiring a 180° twist about bond 4-5. With these changes, mechanism IA leads to overall retention of the original *cis* or *trans* configuration while mechanism IIA results in inversion of the initial geometry. The experimental result of retention of propenyl geometry is consistent only with mechanism IA.

Interestingly, the reaction directionality may also be understood in terms of the orbital representation in Chart III. Thus, to the extent that overlap between orbitals d and e is neglected, one finds a linear sequence of orbitals, namely e-f-a-b-c-d. Since the valence bond picture (Chart II) indicates that C-1-C-3 bonding occurs only in the later stages of the reaction, this approximation is reasonable as long as one is focusing attention on the early portion of the transformation. With such a linear array of orbitals it is clear that maximum stabilization by phenyl substitution will result when these groups are at the *end* of the system, that is at C-1 bearing orbital d, since alternative substitution affords a cross-conjugated excited state and these are generally of higher energy. This reasoning is thus seen to lead to the same observed vinylcyclopro-

(8) J. Hine, *J. Amer. Chem. Soc.*, **88**, 5525 (1966).

(9) Basis orbitals are those used for mixing *via* a secular determinant to give molecular orbitals. The selection of plus and minus orientation is thus arbitrary. However as noted in our earlier papers, in a cyclic array of basis orbitals, the evenness (Hückel systems) or oddness (*i.e.*, Möbius systems<sup>11</sup>) of the number of plus-minus overlaps is characteristic for the system and may be correlated to the final results of molecular orbital mixing. In the case of 18 the basis orbitals constitute a cyclic array (a-b-c-d-e-f)<sup>11</sup> with a single sign change between orbitals f and a and thus is a Möbius system.<sup>11</sup> In 19, the overlap involving orbital d is taken to give a single sign inversion, here between d and e. Since the species are six-electron, six-orbital systems and Möbius-like, both mechanisms IA and IIA are excited state allowed.

(10) Additionally, one might consider "*anti*" conformations rather than the "*syn*" one shown. Similarly, the stereochemistry pictured at C-3 and C-5 in each case is one of two choices. The stereochemistry at C-3 is presently supported only by the one previous case of the di- $\pi$ -methane rearrangement of 1-methylene-4,4-diphenyl-2-cyclohexene.<sup>7</sup> The C-5 stereochemistry is selected to give an allowed process; however, this point is under experimental investigation as is the generality of inversion at C-3.

(11) (a) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564, 1566 (1966); (b) H. E. Zimmerman, *Photochem. Photobiol.*, **7**, 519 (1968); (c) H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969).

pane product **8** (or **9**) as predicted from resonance considerations (*vide supra*).

A final point is of considerable interest, namely the *cis-trans* interconversion exhibited by the triplet excited states of the stereoisomeric diene reactants **5** and **6**. This is related to our earlier observation<sup>6</sup> that the di- $\pi$ -methane rearrangement seems to occur preferentially *via* the singlet excited state for acyclic and other unconstrained systems while utilizing the triplet excited state in constrained molecules such as bicyclic systems. For example, a number of unconstrained di- $\pi$ -methane compounds were found to give unreactive triplets.<sup>1a,6,7</sup> Thus the presently observed *cis-trans* diene interconversion corresponds to hidden processes in the acyclic di- $\pi$ -methanes studied previously, since lack of stereochemistry rendered excited state triplet free rotation unobservable. However, it is presently seen that the presence of an excited state "free rotor" allows triplet energy dissipation,<sup>12</sup> and excited state free rotor effects account for the general failure of acyclic di- $\pi$ -methanes to rearrange by way of their triplets. Bicyclic di- $\pi$ -methane triplets, being geometrically unable to dissipate energy by this free rotor effect, are known to rearrange.

A most interesting facet of this energy dissipation process is the capability of the propenyl moiety to isomerize despite the expectation that the diphenylvinyl group will absorb most of the excitation energy. This may indicate that the triplet counterparts of singlet species **13** and **14** are reached, but that in contrast to the singlet situation these do not rapidly proceed further but rather revert to reactants **5** and **6** following free rotation.

In conclusion, it is noteworthy that the di- $\pi$ -methane rearrangement is proving to be one of the most general, synthetically useful, and mechanistically intriguing of photochemical reactions.

### Experimental Section<sup>13</sup>

***cis*-1,1-Diphenyl-3,3-dimethyl-1,4-hexadiene.** A 54% mineral oil suspension of 8.20 g (184.5 mmol) of sodium hydride was washed three times with dry hexane and blown dry with nitrogen. Dimethyl sulfoxide (40 ml) was added and the mixture was stirred under nitrogen at 70–75° for 1.5 hr and then cooled to room temperature. A solution of 75.00 g (179.3 mmol) of ethyltriphenylphosphonium iodide<sup>14</sup> in 125 ml of dimethyl sulfoxide was added under nitrogen. The deep red color of the ylide appeared immediately and the solution was stirred for 30 min before use.

A solution of 12.3 g (49.2 mmol) of 2,2-dimethyl-4,4-diphenyl-3-butenal<sup>1b,2</sup> in 50 ml of dimethyl sulfoxide was added under nitrogen and the mixture was stirred at 55–60° for 2 hr, then cooled and poured into 1.5 l. of water. The mixture was extracted with hexane and the extract was washed thoroughly with water, dried, and concentrated to ca. 100 ml. The resulting solution was chromatographed on a column (4 cm diameter) which consisted of alumina (Fisher; 37 cm long) topped with deactivated silica gel<sup>15</sup> (15 cm long). Elution was with hexane and the following 1 l. fractions were collected: fractions 1–5, 11.88 g (91%) of a colorless oil; fraction 6 and later fractions were empty. The nmr spectrum of the

oil showed that it was composed of 96% of *cis*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene and 4% of *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene.

The product from the Wittig reaction (1.85 g) was dissolved in 10 ml of hexane and adsorbed on a silica column (Mallinckrodt silicar-CC7; 8 × 86 cm) which had been slurry packed in hexane. Elution was with hexane, the eluent was scanned at 260 m $\mu$ , and the following 40-ml fractions were collected: fractions 1–383, empty; 384–434, 23 mg of unidentified material; 435–441, empty; 442–494, 452 mg of a mixture of *cis*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (84%) and *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (16%); 495–734, 1.29 g of *cis*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene containing none of the *trans* isomer; later fractions were empty.

Fractions 495–734 were distilled under reduced pressure to give pure *cis*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene, bp 122° (0.2 mm). Spectral properties were: ir (CS<sub>2</sub>) 3.23, 3.25, 3.32, 3.37, 3.81, 3.98, 6.28, 7.37, 9.32, 9.70, 13.26, 13.75, and 14.30  $\mu$ ; uv  $\lambda_{\max}^{95\% \text{ EtOH}}$  250 m $\mu$  ( $\epsilon$  13,500); nmr (CCl<sub>4</sub>)  $\tau$  2.89 (m, 10 H, arom), 3.82 (s, 1 H, H-2), 4.80 (m, 2 H, H-4 and H-5), 8.33 (d,  $J$  = 5 cps, 3 H, allylic CH<sub>3</sub>), 8.92 (s, 6 H, *gem*-dimethyl). All efforts to decouple the allylic methyl from the vinyl hydrogens giving rise to the complex multiplet at  $\tau$  4.80 were unsuccessful. Only partial decoupling resulted and no recognizable pattern could be discerned. A number of different solvents were used for determining the nmr spectrum but no simplification of the complex pattern resulted.

*Anal.* Calcd for C<sub>20</sub>H<sub>22</sub>: C, 91.60; H, 8.40. Found: C, 91.18; H, 8.87.

***trans*-1,1-Diphenyl-3,3-dimethyl-1,4-hexadiene.** A solution of 6.00 g (22.9 mmol) of the product from the Wittig reaction and 3.00 g (16.5 mmol) of benzophenone in 200 ml of *t*-butyl alcohol was purged with purified nitrogen<sup>16</sup> for 45 min before and then during irradiation with a 450-W Hanovia medium-pressure mercury lamp through a Pyrex glass filter, all in a water-cooled immersion well, for 3.75 hr. Removal of the solvent *in vacuo* gave a pale yellow oil which was chromatographed on a silica column to remove non-hydrocarbons. The column (Mallinckrodt silicar-CC7; 2 × 60 cm) was slurry packed in hexane. Elution was with hexane and the following 1-l. fractions were collected: fractions 1–2, 4.62 g of a colorless oil, whose nmr spectrum showed it to be a mixture of *cis*- and *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene; fractions 3–5 were empty.

The mixture of the two isomeric hydrocarbons (4.60 g) was chromatographed on a silica column (Mallinckrodt silicar-CC7; 8 × 86 cm) which had been slurry packed in hexane. Elution was with hexane, the eluent was scanned at 260 m $\mu$ , and the following 40-ml fractions were collected: fractions 1–287, empty; 288–359, 5.4 mg of unidentified material; 360–397, 896 mg of *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene which contained none of the *cis* isomer; 398–478, 2.283 g of a mixture of *trans* (85%) and *cis* (15%) dienes; 479–700, 1.267 g of a mixture of the *trans* (24%) and *cis* (76%) dienes; later fractions were empty.

Fractions 360–397 were distilled under reduced pressure to give pure *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene, bp 130° (0.8 mm). Spectral properties were: ir (CS<sub>2</sub>) 3.32, 3.25, 3.30, 3.37, 3.40, 3.49, 6.28, 7.30, 7.40, 9.33, 9.70, 10.11, 10.23, 13.10, 13.25, 13.80, 14.30, and 15.58  $\mu$ ; uv  $\lambda_{\max}^{95\% \text{ EtOH}}$  249 m $\mu$  ( $\epsilon$  13,210); nmr (CCl<sub>4</sub>)  $\tau$  2.88 (m, 10 H, arom), 4.02 (s, 1 H, H-2), 4.78 (m, 2 H, H-4 and H-5), 8.55 (d,  $J$  = 5 cps, 3 H, allylic CH<sub>3</sub>), 8.97 (s, 6 H, *gem*-dimethyl). Efforts were made to decouple the allylic methyl group from the vinyl hydrogens causing the complex multiplet at  $\tau$  4.78. Only partial decoupling resulted and no recognizable simple pattern resulted. Using a wide variety of solvents no simplification of the pattern resulted.

*Anal.* Calcd for C<sub>20</sub>H<sub>22</sub>: C, 91.60; H, 8.40. Found: C, 91.23; H, 8.72.

**Photolysis of *trans*-1,1-Diphenyl-3,3-dimethyl-1,4-hexadiene.** A solution of 591 mg (2.26 mmol) of *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene in 120 ml of *t*-butyl alcohol was purged with purified nitrogen<sup>16</sup> for 45 min before and then during photolysis. Irradiation for 45 min was in the Hanovia apparatus using a Corex glass filter. Removal of the solvent *in vacuo* gave a pale yellow oil which was chromatographed on two preparative thin-layer plates (Brinkmann silica gel GF 254; 20 × 20 cm plates). Four developments with hexane gave two separated bands. The material from each of these was recovered by extraction with ether.

(12) The present results suggest that energy dissipation by free rotation is more characteristic of triplets than of singlets. However, double bond rotation is known to be possible for both singlets and triplets; this point has been discussed in the preceding paper of the series.<sup>1b</sup>

(13) All melting points were determined on a hot-stage apparatus which had been calibrated with known compounds.

(14) A. M. Krubiner and E. P. Oliveto, *J. Org. Chem.*, **31**, 24 (1966).

(15) Deactivated silica gel was prepared by adding 600 g of silica gel (Davison grade 950) to 1200 ml of water with swirling. When cool the silica was filtered off and dried in an oven at 60° for 24 hr before use.

(16) L. Meites, *Anal. Chem.*, **20**, 984 (1948).

The faster moving band yielded 491 mg of a colorless oil. The nmr spectrum showed this oil to be unchanged *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene containing 1-2% of *cis*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene.

The slower moving band gave 102 mg of an oil. The nmr spectrum showed it to be a single vinylcyclopropane isomer with none of the other isomer present in detectable quantities. Recrystallization from methanol gave *trans*-1,1-dimethyl-2,2-diphenyl-3-propenylcyclopropane, mp 57°. Spectral properties were: ir (CS<sub>2</sub>) 3.23, 3.25, 3.30, 3.40, 3.48, 6.28, 7.00, 7.29, 8.68, 8.96, 9.28, 9.78, 10.05, 10.40, 13.04, 13.50, 14.20, 14.41, and 15.87  $\mu$ ; uv  $\lambda_{\max}^{95\% \text{ EtOH}}$  226 m $\mu$  ( $\epsilon$  7210); 100 Mcps<sup>17</sup> nmr (CCl<sub>4</sub>)  $\tau$  2.89 (m, 10 H, arom), 4.35 (d of q's,  $J_d = 15$ ,  $J_q = 6.5$  cps, 1 H, vinyl H at C-2 of the propenyl side chain), 5.08 (d of d of q's,  $J_d = 15$  cps,  $J_d = 10$  cps,  $J_q = 2$  cps approx, 1 H, vinyl H at C-1 of propenyl side chain), 8.02 (d,  $J = 10$  cps, 1 H, cyclopropyl H), 8.31 (d of d's,  $J = 6.5$  cps,  $J = 2$  cps approx, allylic CH<sub>3</sub>), 8.88 (s, 3 H, cyclopropyl CH<sub>3</sub>), and 9.02 (s, 3 H, cyclopropyl CH<sub>3</sub>). Double resonance was performed on the 100-Mcps nmr spectrum. Irradiation of the allylic CH<sub>3</sub> group collapsed H-1 to a doublet of doublets ( $J = 15$  and  $J = 10$  cps). Irradiation of the cyclopropyl H collapsed H-1 to a doublet of doublets ( $J = 15$  and  $J = 2$  cps).

Anal. Calcd for C<sub>20</sub>H<sub>22</sub>: C, 91.60; H, 8.40. Found: C, 91.68; H, 8.53.

**Low-Conversion Photolysis of *cis*-1,1-Diphenyl-3,3-dimethyl-1,4-hexadiene.** A solution of 635 mg (2.24 mmol) of *cis*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene in 120 ml of *t*-butyl alcohol was purged with purified nitrogen<sup>16</sup> for 45 min before and then during the photolysis. Irradiation was with the Hanovia apparatus through a Corex glass filter for 15 min. Removal of the solvent *in vacuo* gave 638 mg of a pale yellow oil which was chromatographed on a silica preparative thin-layer plate. Five developments with hexane gave two separated bands. The material from these bands was removed by extraction with ether.

The faster moving band yielded 572 mg of a colorless oil, the nmr spectrum showing it to consist of unchanged *cis*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene containing 3% of the *trans* diene.

The slower moving band gave 57 mg of a colorless oil. The nmr spectrum showed it to consist of a single vinylcyclopropane isomer, the other isomer not being present in detectable quantities. The oil was purified by molecular distillation at 100° (0.1 mm) to give pure *cis*-1,1-dimethyl-2,2-diphenyl-3-propenylcyclopropane. Spectral properties were: ir (CS<sub>2</sub>) 3.23, 3.26, 3.29, 3.36, 3.40, 3.42, 3.49, 6.28, 7.00, 7.29, 8.96, 9.31, 9.78, 13.24, 13.48, 14.20, 14.40, 14.71, and 15.98  $\mu$ ; uv  $\lambda_{\max}^{95\% \text{ EtOH}}$  227 m $\mu$  ( $\epsilon$  7420); 100 Mcps nmr (CCl<sub>4</sub>)  $\tau$  2.88 (m, 10 H, arom), 4.47 (d of q's,  $J_d = 11$ ,  $J_q = 6$  cps, 1 H, vinyl hydrogen at C-2 of the propenyl side chain), 5.07 (d of d of q's,  $J_d = 10$ ,  $J_d = 11$ ,  $J_q = 2$  cps approx, 1 H, vinyl H at C-1 of the propenyl side chain), 7.80 (d,  $J = 10$  cps, 1 H, cyclopropyl H), 8.14 (d of d,  $J = 6$  cps,  $J = 2$  cps approx, 3 H, allylic CH<sub>3</sub>), 8.90 (s, 3 H, cyclopropyl CH<sub>3</sub>), and 8.98 (s, 3 H, cyclopropyl CH<sub>3</sub>). Double resonance was performed on the 100 Mcps spectrum. Irradiation of the allylic methyl group collapsed H-1 to a doublet of doublets

( $J = 10$  and  $J = 11$  cps). Irradiation of the cyclopropyl H collapsed H-1 to a doublet of quartets ( $J_d = 11$  and  $J_q = 2$  cps approx).

Anal. Calcd for C<sub>20</sub>H<sub>22</sub>: C, 91.60; H, 8.40. Found: C, 91.56; H, 8.40.

**Higher Conversion Photolysis of *cis*-1,1-Diphenyl-3,3-dimethyl-1,4-hexadiene.** A solution of 684 mg (2.61 mmol) of *cis*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene in 120 ml of *t*-butyl alcohol was purged with purified nitrogen<sup>16</sup> for 45 min before and then during photolysis. Irradiation was for 40 min in the Hanovia apparatus using a Corex glass filter. Removal of the solvent *in vacuo* gave a pale yellow oil which was chromatographed on two silica preparative thin-layer plates. Five developments with hexane gave two separated bands. The material from each was recovered by ether extraction.

The faster moving band yielded 516 mg of a colorless oil. The nmr spectrum of the oil showed it to consist of a mixture of *cis*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (83%) and *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (17%).

The slower moving band yielded 160 mg of a colorless oil whose nmr spectrum (HA-100 Mcps spectrum) indicated that it was a mixture of *cis*-1,1-dimethyl-2,2-diphenyl-3-propenylcyclopropane (~65%) and *trans*-1,1-dimethyl-2,2-diphenyl-3-propenylcyclopropane (~35%).

**Benzophenone-Sensitized Photolysis of *cis*-1,1-Diphenyl-3,3-dimethyl-1,4-hexadiene.** A solution containing 500 mg (1.91 mmol) of *cis*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene and 2.00 g (19.05 mmol) of benzophenone in 120 ml of *t*-butyl alcohol was purged with purified nitrogen<sup>16</sup> for 45 min before and then during photolysis. Irradiation was for 1 hr through a Pyrex glass filter in the Hanovia apparatus. Removal of the solvent *in vacuo* gave 2.46 g of a pale yellow oil. A 500-mg portion of this oil was chromatographed on a silica preparative thin-layer plate. After two developments two bands had separated. Recovery of the material from the faster moving band by ether extraction gave 92 mg of an oil whose nmr spectrum showed it to be *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene containing 3% of *cis*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene. The slower moving band yielded 357 mg of benzophenone.

**Benzophenone-Sensitized Photolysis of *trans*-1,1-Diphenyl-3,3-dimethyl-1,4-hexadiene.** A solution containing 500 mg (1.91 mmol) of *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene and 2.00 g (19.05 mmol) of benzophenone in 120 ml of *t*-butyl alcohol was purged with purified nitrogen<sup>16</sup> for 45 min before and then during photolysis. Irradiation was for 1 hr through a Pyrex glass filter in the Hanovia apparatus. Removal of the solvent *in vacuo* gave 2.41 g of a pale yellow oil. A 500-mg portion of the oil was chromatographed on a silica preparative thin-layer plate. Two developments with hexane separated the material into two bands. Recovery of the material from the first band by ether extraction gave 89 mg of an oil. The nmr spectrum showed it to be unchanged *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene containing 2-3% of the *cis* diene.

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