

the U. S. Army Research Office (Durham) is gratefully acknowledged.

Howard E. Zimmerman, Albert C. Pratt  
 Chemistry Department, University of Wisconsin  
 Madison, Wisconsin 53706  
 Received November 14, 1969

**Organic Photochemistry. LIV.<sup>1</sup>**  
**Concertedness, Stereochemistry, and Energy Dissipation**  
**in the Di- $\pi$ -methane Rearrangement. Source of**  
**Singlet-Triplet Reactivity Differences**

Sir:

Previously, in noting the generality of the di- $\pi$ -methane rearrangement, we suggested that bicyclic di- $\pi$ -methanes rearrange by way of triplet excited states in contrast to the acyclic di- $\pi$ -methanes where the singlet reacts smoothly and where the triplet excited state is either totally or nearly totally unreactive.

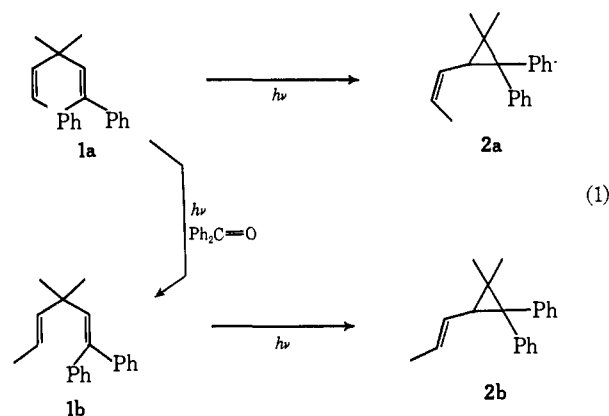
We now report evidence (a) which clearly demonstrates the reason for this difference in reactivity, (b) which delineates an important part of the di- $\pi$ -methane reaction stereochemistry, and (c) which reveals a hidden energy dissipation process in the triplet photochemistry of certain of these systems.

We synthesized the *cis*- and *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadienes (**1a** and **1b**, respectively).<sup>2</sup> The *cis* isomer **1a** was obtained from the Wittig reaction of ethylenetriphenylphosphorane with the known<sup>3</sup> 2,2-dimethyl-4,4-diphenyl-3-butenal. The preferential formation of the *cis* stereoisomer is expected from literature investigations<sup>4</sup> of the reaction. The *trans* isomer **1b** was obtained from the benzophenone-sensitized irradiation of **1a**.

The stereochemistry of the isomers **1a** and **1b** was most clearly defined from their infrared spectra. The *trans* isomer had a strong absorption band at 10.33  $\mu$  (968  $\text{cm}^{-1}$ ) characteristic of *trans*-disubstituted olefins and also present in other *trans* compounds in this study. No corresponding absorption was found in the 9.8–12.5- $\mu$  (800–1020  $\text{cm}^{-1}$ ) region of the *cis* compound **1a**.

Direct irradiation of *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (**1b**) afforded one product, **2b**, cleanly in a preparatively useful reaction. Unreacted *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (**1b**) was recovered with inappreciable (<3%) stereoisomerization to *cis*-diene **1a**. Similar direct irradiation of *cis*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (**1a**) afforded a single product, **2a**, different from **2b**, in low conversion (*i.e.*, *ca.* 10%) runs, and only *ca.* 3% diene stereoisomerization was noted. The structures of the photoproducts (**2a** and **2b**) were established unambiguously by nmr, as the *cis*- and *trans*-1,1-dimethyl-2,2-diphenyl-3-propenylcyclopropane stereoisomers. In each case absorption was observed deriving from two nonequivalent unsplit methyl groups ( $\tau$  8.90 and 8.98 in **2a** and 8.88 and 9.02 in **2b**), an allylic methyl group ( $\tau$  8.14 in **2a** and 8.31 in **2b**) split by coupling with an adjacent

vinyl group ( $J = 6$  cps) and an allylic vinyl hydrogen ( $J = 2$  cps), a cyclopropyl methine ( $\tau$  7.80 in **2a** and 8.02 in **2b**) split ( $J = 10$  cps) into a doublet by an adjacent vinyl hydrogen, two vinyl hydrogens ( $\tau$  4.47, doublet of quartets,  $J = 6.0$  (q) and 11 cps (d), 5.07, doublet of doublet of quartets,  $J = 11$  (d), 10 (d), and 2 cps (q) in **2a**; and in **2b**  $\tau$  4.35, doublet of quartets,  $J = 6.5$  (q) and 15 cps (d), 5.08, doublet of doublet of quartets,  $J = 15$  (d), 10 (d), and 2 cps (q)) as part of a CHCH=CHCH<sub>3</sub> moiety, and ten aromatic hydrogens at  $\tau$  2.89. The configurational assignments derive from the large (*i.e.*, 15-cps) vinyl-vinyl coupling constant for **2b** as expected for *trans* ethylenic hydrogens and the smaller 11-cps coupling expected and found for the *cis* stereoisomer **2a**. This assignment was confirmed by the absence of *trans* C-H out-of-plane bending absorption in the 10–12- $\mu$  (780–1000  $\text{cm}^{-1}$ ) region of the ir of **2a** contrasted with the strong characteristic 10.4- $\mu$  (960  $\text{cm}^{-1}$ ) band found for the *trans* stereoisomer **2b**. Hence, the reaction proved to be stereospecific and led to retention of the original double bond configuration (see eq 1).



Evidence that this stereospecific process derived from the singlet excited state came from sensitization experiments. Under reaction conditions designed to allow efficient triplet but no singlet energy transfer, benzophenone sensitization of either *cis*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (**1a**) or the *trans*-diene **1b** resulted in no di- $\pi$ -methane rearrangement. Rather *cis*-*trans* isomerization occurred with a steady state of 97% *trans*-diene **1b** and 3% *cis*-diene **1a**.

The di- $\pi$ -methane reaction of **1a** and **1b** can be seen to result from only one of the two *a priori* available pathways in Chart I, namely route A. This preference has analogy in our report on the directionality of the di- $\pi$ -methane rearrangement<sup>1a</sup> and is attributed to the greater electron density at C-5 in species **4a** than at C-1 as a result of benzhydryl delocalization. Density at C-5 is needed for bond-3,4 fission (arrows a) while electron density at C-1 is required for bond-2,3 cleavage. The same selectivity encountered in the rearrangement of *trans*-diene **1b** is similarly understood.

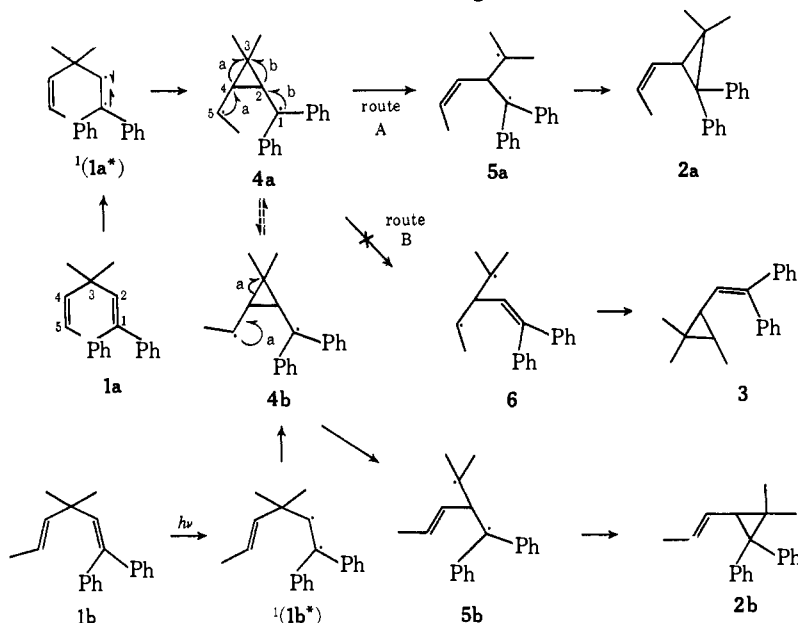
Thus electron delocalization in species **4a** and **4b** accounts for the reaction directionality. However, these species cannot be long-lived intermediates since rotation about bond 4,5 would then allow interconversion of **4a** and **4b** with loss of stereospecificity of the reaction. The species **4a** and **4b** in Chart I, as well as the other biradical-like entities shown, probably then represent points on an excited-state potential-energy

(1) (a) For paper LIII of the series see H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **92**, 1407 (1970); (b) paper LII: H. E. Zimmerman and H. Iwamura, *ibid.*, in press.

(2) (a) All compounds analyzed acceptably. Full experimental details will be presented in our full publication. (b) Irradiations were carried out in a medium-pressure immersion lamp apparatus.

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

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

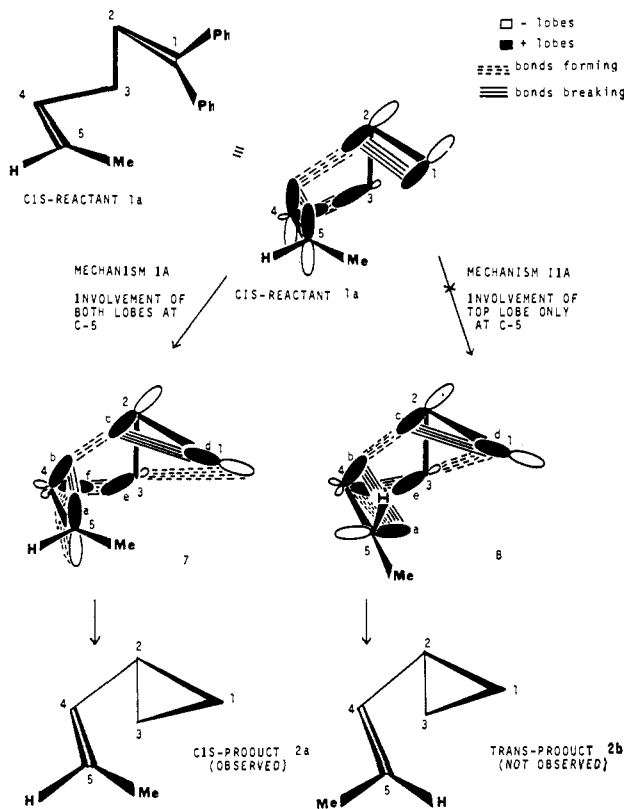
**Chart I.** Potential and Utilized Mechanisms in the Di- $\pi$ -methane Rearrangements of **1a** and **1b**

surface. A minimum interpretation requires that the rate of rotation of **4a** and **4b** be slower than ring opening. To the extent that rotation is impeded by odd electron delocalization into the three-membered ring, this merely represents the beginning of the ring-opening process.

The observation of *cis*-diene-*trans*-diene interconversion of the triplet rather than di- $\pi$ -methane rearrangement corresponds to hidden processes in the acyclic di- $\pi$ -methanes studied previously<sup>5</sup> since lack of stereochemistry rendered excited-state free rotation unobservable. This process allows triplet energy dissipation and accounts for the general failure of acyclic di- $\pi$ -methanes to rearrange *via* their triplets. Bicyclic di- $\pi$ -methane triplets, being geometrically unable to dissipate energy by this "free rotor" effect, are known<sup>6</sup> to rearrange. This difference depending on excited-state multiplicity suggests either that the excited singlets have less driving force for free rotation than the triplets or that the di- $\pi$ -methane process is particularly facile for the singlet.

An interesting facet of the triplet *cis*-*trans* isomerization is the ability of the high-energy propenyl moiety to isomerize despite the expectation that the diphenylvinyl group will absorb most of the excitation energy. This may indicate that species such as **4a** and **4b** are reached, but that in contrast to the singlet situation these do not rapidly proceed further.

Finally, the present results establish the stereochemistry at still another center in the di- $\pi$ -methane process. Previous results indicated<sup>5b</sup> a preference for inversion at C-3. The present results reveal the preference for the stereochemistry at C-5 as shown in Chart II which depicts the orbital and molecular change as the reaction proceeds. It is seen that both lobes are utilized as in **7** rather than just one lobe as in **8**. The latter would lead to inversion of the isopropenyl con-

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

figuration. This fits theoretical expectation<sup>5a</sup> for a six-electron, six-orbital excited state if the stereochemistry at C-1 is disrotatory relative to C-3. This point is being tested.

**Acknowledgment.** Support of this research by NIH Grant GM07487 and the U. S. Army Research Office (Durham) is gratefully acknowledged.

Howard E. Zimmerman, Albert C. Pratt  
Chemistry Department, University of Wisconsin  
Madison, Wisconsin 53706  
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(5) (a) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969); (b) H. E. Zimmerman and G. E. Samuelson, *ibid.*, **89**, 5971 (1967); **91**, 5307 (1969).

(6) (a) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); **91**, 3316 (1969); (b) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 4191 (1968); **91**, 6096 (1969).