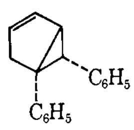
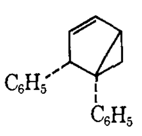


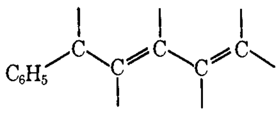
VII



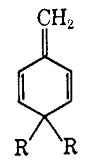
VIII

indicated that within the limits of experimental error (1%) the *cis* isomers were not detected.

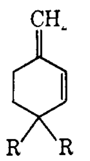
The facile triplet-state rearrangement of I contrasts with the inertness of the triplet states of general structure IX, X, and XI.[2,13] Since the present results indicate the triplet state of a diene–phenyl moiety is capable of the di-π-methane rearrangement, the low reactivity of the above systems is not due to the inherent reactivity of the diene triplet. Rather we believe that the lack of reactivity in systems capable of rotational freedom results from facile deactivation of the triplet as a consequence of rotation about the carbon–carbon linkage(s).[14]



IX



X



XI

The nearly complete absence of products having the phenyl groups *cis* from photolysis of I corresponds to previous results in other systems.[2] Possibly, spin inversion in the triplet occurs in the half-bridged species with resultant cyclopropane formation being nearly concerted with the completion of phenyl migration. The 90:10 stereoselectivity observed in this photoprocess could reflect either kinetic or thermodynamic product control.[15] Thermolysis of either II or III in cyclohexane at 130, 160, or 190° yielded nearly the same equilibrium mixture of II (60 ± 1%) and III (40 ± 1%).[16] The small temperature dependence of the II–III equilibrium indicates that the 90:10 ratio observed photochemically reflects some kinetic aspect of product formation in the excited state. While this may be a consequence of the geometry of the excited diene triplet, further speculation at this time is unwarranted.[17]

Acknowledgment. We are thankful to the Eli Lilly Company whose financial assistance supported this research.

---

sequence as utilized for III employing the epimer of IV. The vpc retention times (0.125 in. × 5 ft 5% SE-30 on 100–120 mesh Varaport 30, injection temperature 160°, column temperature 145°) were as follows: *cis*-4,5-diphenyl-, 8.5 min; *cis*-5,6-diphenyl-, 10.5 min; *trans*-4,5-diphenyl-, 11.5 min; *trans*-5,6-diphenylbicyclo[3.1.0]hex-2-ene, 12.5 min.

[13] (a) W. G. Dauben and W. A. Spitzer, *J. Amer. Chem. Soc.*, **90**, 803 (1968); (b) H. Hart, J. D. DeVrieze, R. H. Lange, and A. Sheller, *Chem. Commun.*, 1650 (1968).

[14] *A priori* the singlet state of the diene is also subject to deactivation by rotation; one might inquire why reaction occurs at all. First, little experimental evidence is available to establish rotation is a facile process in the excited singlet state of olefins. In fact, *cis–trans* isomerization is characteristically a triplet-state reaction. A second rationale applicable to the phenyl-substituted systems is that the singlet energy in these systems is largely localized in the aromatic residue. In this case the reaction would arise from attack of the aromatic ring on the diene system.

[15] The formation of III does not result from further photochemical transformation of II. While III is stable under 2-acetonaphthone sensitization, *m*-methoxyacetophenone sensitization results in photoisomerization to VII.

[16] Small amounts of the *cis* isomers were also formed in these thermolyses. The thermolyses of photochemical transformations of these olefins will be the subject of a future publication.

[17] New compounds reported here have been characterized by acceptable combustion analyses and ir and nmr spectra (IV by exact mass measurement and ir and nmr spectra). Due to the large numbers of new compounds, delineation of spectroscopic data will be deferred to our full paper.

[18] (a) National Science Foundation Undergraduate Research Participant, 1969; (b) Undergraduate Research Participant.

John S. Swenton, Ann R. Crumrine,[18a] Timothy J. Walker[18b]
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received November 14, 1969

Organic Photochemistry. LIII.[1]
Directionality of the Singlet Di-π-methane. Rearrangement and Alkyl Migration in a Unique Photochemical Vinylcyclopropane Transformation

Sir:

Previously we reported[2] on the generality of the di-π-methane rearrangement. We now wish to communicate some findings bearing on the nature of this transformation and also on the differing reactivity of singlet *vs.* triplet excited states. We find: (a) the direction of the di-π-methane rearrangement is controlled by demand of the excited state for retention of maximum electron delocalization during the rearrangement; (b) support for the diradicaloid mechanism tentatively advanced by us earlier; (c) further evidence that acyclic di-π-methane triplets are unreactive in contrast to the singlets; (d) a surprising observation bearing on the effect of structure on reaction efficiency; and (e) a unique rearrangement of a vinylcyclopropane derivative.

To determine the nature of the excited-state rearrangement of di-π-methanes and provide information needed for subsequent stereochemical studies, we investigated the role of substitution on direction of rearrangement. Thus, the direct photolysis[3] of 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene (**1**), bp 131° (0.2 mm),[3] afforded only one of the two *a priori* possible di-π-methane rearrangement products **2** and **3** (note Chart I). Only 1,1-dimethyl-2,2-diphenyl-3-(2-methylpropenyl)cyclopropane (**2**), mp 77°, was formed. In one typical run, 2.00 g of reactant afforded in 3 hr 1.52 g of vinylcyclopropane **2** and 0.55 g of recovered divinylmethane **1**.

The product structure was suggested by the nmr spectrum. This had a vinyl region consisting of a doublet of multiplets at τ 5.27 (J = 9 cps) and deriving from a single proton. A τ 7.93 methine doublet was coupled (J = 9 cps) to the vinyl. 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); these were attributed to nonequivalent allylic methyls, each coupled to the vinyl proton. Finally, the structure of **2** was firmly established by

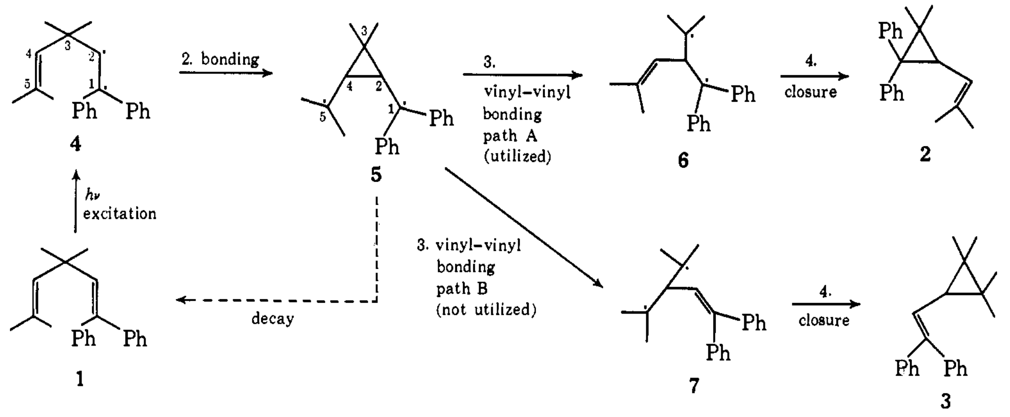
---

[1] For paper LII of the series see: H. E. Zimmerman and H. Iwamura, *J. Amer. Chem. Soc.*, in press.

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

[3] (a) Full experimental and synthetic detail will be found in our full paper. (b) Irradiations were carried out with the "black box" 1000-W apparatus using filter solutions described previously (H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966)).

Chart I. Valence Bond Representation of Reaction Selectivity



oxidative degradation to the known[2] 2,2-dimethyl-3,3-diphenylcyclopropanecarboxylic acid.[3] Independent synthesis of **3** allowed demonstration that its photolysis products were not present in the irradiation runs and that **3** was not converted to **2** or to other compounds encountered under photolysis conditions.

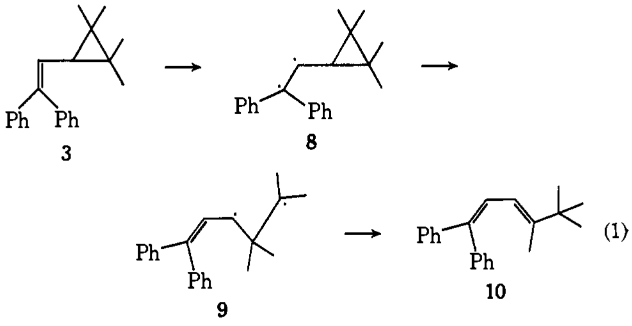
Quantum yields were determined with and without benzophenone as sensitizer. The unsensitized quantum yield was $\Phi = 0.097 \pm 0.007$, indicating a relatively efficient and useful reaction. With benzophenone, under conditions allowing only triplet transfer and with sensitizer absorbing over 98% of the light, a quantum yield of $\Phi(\text{sens}) = 0.008 \pm 0.002$ was obtained. Mass balances were 97–99%. Runs with benzhydrol and benzophenone present showed that the divinylmethane **1** quenched benzopinacolization and therefore demonstrated that triplet transfer to diene was indeed occurring.

Hence the reaction is a singlet process. The triplet, when generated, reacts only inefficiently. This is in accord with our previous observations and tentative generalization[2,4] that bicyclic di-π-methanes react *via* triplets while acyclic di-π-methanes prefer singlet pathways.

The marked selectivity in which only pathway A, and not B, is followed in the di-π-methane transformation (note Chart I) indicates that appreciable free valences develop in the excited-state species during the product-controlling stages of the rearrangement. This corresponds to process 3 in Chart I. Consideration of 1,4-biradicaloid species[5] **5** in Chart I leads to the conclusion that, to the extent that delocalization maximization is favored on the excited state[6] potential energy surface, process A will least localize odd electrons. Thus, the odd-electron at the benzhydryl center C-1 is diffuse and relatively unavailable for the cyclopropylcarbinyl to allylcarbinyl fission process 3. In contrast, the odd electron of C-5 is heavily localized. This then accords with our view that many photochemical processes are controlled by energy minimization and thus electron-localization minimization.[8]

Finally, with respect to the di-π-methane rearrangement of **1**, we find a remarkably similar efficiency quantum yield ($\Phi = 0.097$) compared to the efficiency ($\Phi = 0.080$) for the symmetrically substituted 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene studied by us earlier.[2] In view of the effect of methyl *vs.* phenyl substitution on the direction of rearrangement, one might *a priori* have expected an effect of substitution on the probability of rearrangement. The simplest rationale is that the excited-state decay rate of a species such as **5** (by bond-2,4 fission) is affected to the same extent by change in substitution as the rate of bond-3,4 fission. This is reasonable since both are cyclopropylcarbinyl cleavages. A parallel change in decay and reaction rates will keep the quantum yield constant.

In conclusion, we report the unusual rearrangement of vinylcyclopropane **3** on direct photolysis to give 1,1-diphenyl-4,5,5-trimethyl-1,3-hexadiene (**10**), as shown in eq 1. This 1,3-biradicaloid rearrangement has little precedent and seems to occur only where disengagement[9] of a relatively stable carbene is structurally not possible.



(1)

Acknowledgments. Support of this research by the National Institutes of Health, Grant GM07487, and

---

(4) (a) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **91**, 3316 (1969); (b) H. E. Zimmerman and G. L. Samuelson, *ibid.*, **91**, 5307 (1969); (c) H. E. Zimmerman, R. M. Pagni, and R. S. Givens, *ibid.*, **90**, 6096 (1968).

(5) The species depicted in Chart I are shown for convenience and represent molecules in transit reacting along an excited-state potential-energy surface; that these are not long-lived intermediates is clear from the accompanying communication (H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 1409 (1970)).

(6) That species **5** is still electronically excited derives from unpublished results by H. E. Zimmerman and R. J. Boettcher as well as the general observation[7] that such 1,4-biradical-like systems, when generated thermally, tend to afford 1,4-dienes rather than vinylcyclopropanes.

(7) (a) For a leading reference see J. A. Berson and S. S. Olin, *ibid.*, **91**, 777 (1969); (b) we acknowledge with pleasure discussions of the point with Professor Berson.

(8) (a) H. E. Zimmerman, 17th National Organic Symposium Abstracts, Bloomington, Ind., June 1960, p 31; (b) *Advan. Photochem.*, **1**, 183 (1963); (c) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962); **83**, 4486 (1961).

(9) Note the contrasting photochemical formation of carbene from cyclopropanes described by H. Kristinsson, K. N. Mehrota, G. W. Griffin, R. C. Petterson, and C. S. Irving, *Chem. Ind.* (London), 1562 (1966). Similarly, cyclopropane **2** affords carbene fission; these details will be described in our full paper.

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.[1] Concertedness, Stereochemistry, and Energy Dissipation in the Di-π-methane Rearrangement. Source of Singlet–Triplet Reactivity Differences

Sir:

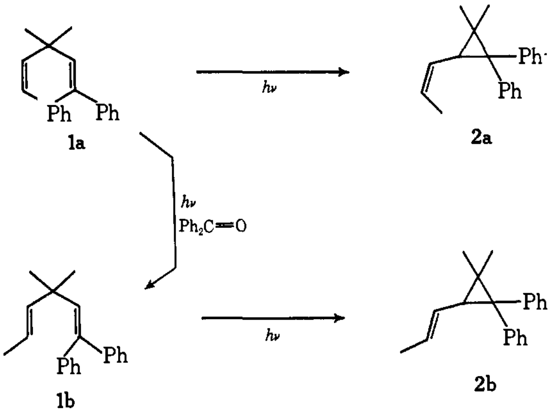
Previously, in noting the generality of the di-π-methane rearrangement, we suggested that bicyclic di-π-methanes rearrange by way of triplet excited states in contrast to the acyclic di-π-methanes where the singlet reacts smoothly and where the triplet excited state is either totally or nearly totally 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-π-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).[2] The *cis* isomer **1a** was obtained from the Wittig reaction of ethylidenetriphenylphosphorane with the known[3] 2,2-dimethyl-4,4-diphenyl-3-butenal. The preferential formation of the *cis* stereoisomer is expected from literature investigations[4] 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 μ (968 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-μ (800–1020 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 (τ 8.90 and 8.98 in **2a** and 8.88 and 9.02 in **2b**), an allylic methyl group (τ 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 (τ 7.80 in **2a** and 8.02 in **2b**) split (J = 10 cps) into a doublet by an adjacent vinyl hydrogen, two vinyl hydrogens (τ 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** τ 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 $CHCH{=}CHCH_3$ moiety, and ten aromatic hydrogens at τ 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-μ (780–1000 cm^{-1}) region of the ir of **2a** contrasted with the strong characteristic 10.4-μ (960 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).



(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-π-methane rearrangement. Rather *cis–trans* isomerization occurred with a steady state of 97% *trans*-diene **1b** and 3% *cis*-diene **1a**.

The di-π-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-π-methane rearrangement[1a] 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).