toward return to II but reacts as a typical 1,3 dipole. Colored intermediates have been observed upon irradiation of monocyclic aryloxiranes only at low temperatures (77°K). The proposed structures in these cases result from carbon–oxygen bond cleavage.[5b,18] Similarly, irradiation of monocyclic aryloxiranes in alcoholic solution affords products from carbon–oxygen bond cleavage.[19,20] Dark reactions involving central bond cleavage of oxiranes have been reported previously.[6e–j,17b–d]

Acknowledgment. We are grateful to Dr. E. B. Whipple and M. Ruta for assistance with the nmr experiments and to Dr. P. Kasai for carrying out the esr measurements.

(18) It has now been shown that the carbon–carbon bond is cleaved in these intermediates (T. Do-Minh, A. M. Trozzolo, and G. W. Griffin, *J. Amer. Chem. Soc.*, **92**, 1402 (1970)).

(19) R. C. Petterson, C. S. Irving, A. M. Khan, G. W. Griffin, and I. M. Sarkar, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., 1969, No. ORGN 10; K. Tokumaru, *Bull. Chem. Soc., Jap.*, **40**, 242 (1967).

(20) Dr. Paul Kropp has shown that these additions are acid-catalyzed dark reactions following the formation of acid upon irradiation (Hanovia Photochemical Symposium, Chicago, Ill., Oct 1969).

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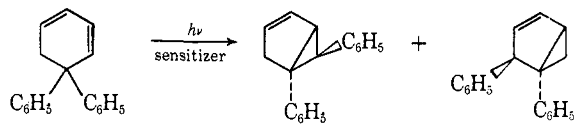
Geometric Factors in Multiplicity-Dependent Photochemistry. Intramolecular Triplet-State Rearrangement of 5,5-Diphenyl-1,3-cyclohexadiene

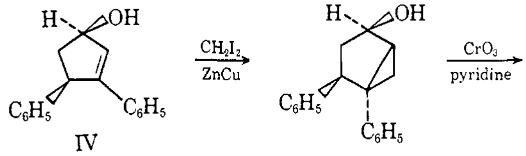
Sir:

An interesting mechanistic aspect of the di-π-methane–vinylcyclopropane rearrangement is the dependence of the multiplicity of the process on the structural character of the substrate.[1] Molecules having the possibility of rotational freedom in the excited state (*i.e.*, acyclic dienes and dienes having exocyclic methylene groups) undergo rearrangement most efficiently in the excited singlet state,[2] whereas systems possessing geometric constraints to rotation prefer to undergo reaction in the triplet state.[3,4] Our interest in the importance of excited-state geometry in modifying the photochemical and photophysical processes of the excited state[5] led us to surmise that the generalizations noted above resulted from conformational effects in the excited state.[6] To test this idea we chose for study 5,5-diphenylcyclohexa-1,3-diene (I). The cyclohexadiene skeleton can accommodate limited twisting about the carbon–carbon linkages, yet free rotation about any of the ring bonds appears unlikely.

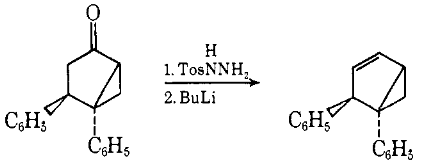
Sensitized irradiation of I in benzene using fluorenone (E_T = 53.3 kcal/mol), 2-acetonaphthone (E_T = 59.6 kcal/mol), or Michler's ketone (E_T = 61 kcal/mol) as sensitizer[7] yielded two monomeric products in a ratio of 91:9 (80–90% yield).[8] The major product was isolated by chromatography and identified as *trans*-5,6-diphenylbicyclo[3.1.0]hex-2-ene (II) by comparison with authentic material.[9] The minor product was isolated by a combination of column and vapor phase chromatography and its identity was established as *trans*-4,5-diphenylbicyclo[3.1.0]hex-2-ene (III) by comparison with synthetic material (*vide infra*).[11] To add credibility to the marked stereoselectivity observed in the photoprocess, the *cis* isomers VII and VIII were prepared.[12] Vapor-phase analysis of the reaction mixture



I II III



IV V



VI III

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(1) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969).

(2) (a) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *ibid.*, **87**, 1410 (1965); (b) H. Kristinsson and G. S. Hammond, *ibid.*, **89**, 5968 (1967); (c) H. E. Zimmerman and G. E. Samuelson, *ibid.*, **89**, 5971 (1967); **91**, 5307 (1969); (d) H. E. Zimmerman, P. Hackett, D. F. Juers, and B. Schröder, *ibid.*, **89**, 5973 (1967); (e) E. C. Sanford and G. S. Hammond, Western Regional Meeting of the American Chemical Society, Anaheim, Calif., Oct 6, 1969, Paper 63.

(3) (a) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 2882 (1966); (b) J. R. Edman, *ibid.*, **88**, 3454 (1966); (c) H. E. R. Zimmerman, W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); (d) J. Brewer and H. Heaney, *Chem. Commun.*, 811 (1967); (e) P. Rabideau, J. B. Hamilton, and L. Friedman, *J. Amer. Chem. Soc.*, **90**, 4466 (1968); (f) R. S. H. Liu, *ibid.*, **90**, 215 (1968); (g) H. Hart and R. K. Murray, *ibid.*, **91**, 2183 (1969).

(4) Two recent examples not in complete accord with these generalizations are: (a) R. C. Hahn and L. J. Rothman, *ibid.*, **91**, 2409 (1969); (b) S. J. Cristol and G. O. Mayo, *J. Org. Chem.*, **34**, 2363 (1969).

(5) A discussion on the importance of geometric change in the photochemistry of biaryls has been presented: J. S. Swenton, B. H. Williams, and T. Ikeler, Symposium on Excited State Chemistry, Western Regional Meeting of the American Chemical Society, Anaheim, Calif., Oct 7, 1969, Paper 104.

(6) The low reactivity of the acyclic and exocyclic olefins would result from rotation about bonds of low π-bond order in the excited state affording a facile pathway for loss of electronic energy. In the more rigid systems this mode of energy dissipation would not be available; thus these molecules would have maximum opportunity for rearrangement.

(7) Photolyses were carried out on 0.3 g of diene and 0.3 g of sensitizer in 150 ml of benzene using Pyrex-filtered light from a 450-W medium-pressure source. The starting material was completely converted in 0.5 hr. Yields were determined by vpc using fluorenone or 2-acetonaphthone as internal standards. The ratios of II and III from vpc and nmr determination were within ±1%. Preliminary results using acetone as sensitizer resulted in formation of three major products: II (75%), III (7%), and VII (18%).

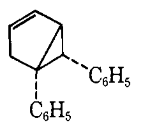
(8) Preliminary preparative irradiations of I in cyclohexane at 2537 Å yielded no detectable amounts of II or III. One of the singlet products has been identified as 1,1-diphenyl-1,3,5-hexatriene on the basis of its hydrogenation to 1,1-diphenylhexane.

(9) The authentic material was synthesized using the Shapiro–Shechter–Dauben[10] method from the known *trans* ketone [H. E. Zimmerman and J. W. Wilson, *J. Amer. Chem. Soc.*, **86**, 4036 (1964)]. The olefin II, mp 56–57°, had the expected ir and nmr spectra.

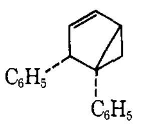
(10) (a) R. H. Shapiro and M. J. Heath, *ibid.*, **89**, 5734 (1967); (b) G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967); (c) W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *ibid.*, **90**, 4762 (1968).

(11) The alcohol IV was prepared by reduction of 3,4-diphenylcyclopent-2-en-1-one using either sodium borohydride or the Meerwein–Ponndorf–Verley reduction. The ratio of IV and its epimer obtained from sodium borohydride reduction was 75:25 while MPV reduction yielded a ratio of 33:67. Note that the MPV results are in disagreement with those obtained by P. Bladon, S. McVey, P. L. Pauson, G. D. Broadhead, and W. M. Horspool, *J. Chem. Soc., C*, 306 (1966). The *trans* olefin III was obtained as a clear oil showing the expected ir and nmr absorptions.

(12) The *cis*-5,6-diphenylbicyclo[3.1.0]hex-2-ene (VII) was prepared from the corresponding ketone[9] and had mp 69–70°. The *cis*-4,5-diphenyl[3.1.0]hex-2-ene, mp 58–59° (VIII), was prepared by the same



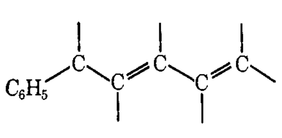
VII



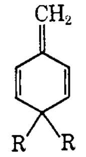
VIII

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

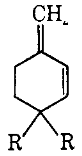
The facile triplet-state rearrangement of I contrasts with the inertness of the triplet states of general structure



IX



X



XI

ture 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]

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.

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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.

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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

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(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)).