involving coordination solely with the olefinic double bond.[8]

If it is assumed that the iron atom in **3**, aided by the triphenylphosphine ligand, donates two electrons to the thioacrolein ligand, HMO calculations on dinegative thioacrolein ($\alpha_S = \alpha_C + 1.5\beta_{CC}$, $\beta_{CS} = 0.5\beta_{CC}$) predict bond orders (C–S, 1.09; C_1–C_2, 1.72; C_2–C_3, 1.68) which are qualitatively in agreement with approximate bond orders derived from the bond distances in **3** (C–S, 1.1; C_1–C_2, 2; C_2–C_3, 1.7). Essentially a full negative charge is predicted on sulfur, in agreement with its facile oxidation, and the second negative charge is predicted to be distributed principally between C_1 and C_3. In agreement with the latter prediction, the protons on C_1 and C_3 in **3** are more shielded (δ 6.10, 1.95, and 0.90, respectively) in the complex than they are in thiete (δ 6.50 and 3.80, respectively). The shielding of the proton on C_2 is unchanged (δ 5.60).

Acknowledgments. We are grateful to the National Science Foundation (Grant GP 20729) and the National Cancer Institute of the Public Health Service (Grant CA 08250) for partial financial support of this work. We are indebted to Professor W. A. Baker, Alan Blumenthal, David Ford, and Michael Villareale for assistance in obtaining the Mössbauer parameters and to Dr. George C. Levy for the decoupling of protons in **3** in order to reveal the coupling with phosphorus.

---

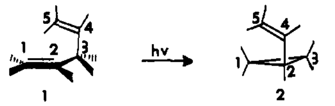
[8] E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963). Molybdenum, rhodium, and nickel complexes of acrolein apparently involve coordination also with the carbonyl group: D. P. Tate, A. A. Buss, J. M. Augl, B. L. Ross, J. G. Grasselli, W. M. Ritchey, and F. J. Knoll, *Inorg. Chem.*, **4**, 1323 (1965); M. Hidai, K. Ishimi, M. Iwasa, and Y. Uchida, *Bull. Chem. Soc. Jap.*, **45**, 2935 (1972); G. N. Schrauzer, *Chem. Ber.*, **94**, 642 (1961).

K. Takahashi, M. Iwanami, A. Tsai
P. L. Chang, R. L. Harlow, L. E. Harris
J. E. McCaskie, C. E. Pfluger, D. C. Dittmer*
Department of Chemistry, Syracuse University
Syracuse, New York 13210
Received June 21, 1973

Di-π-methane Stereochemistry. The Effect of Structural Limitations Which Preclude Preferred Modes[1]

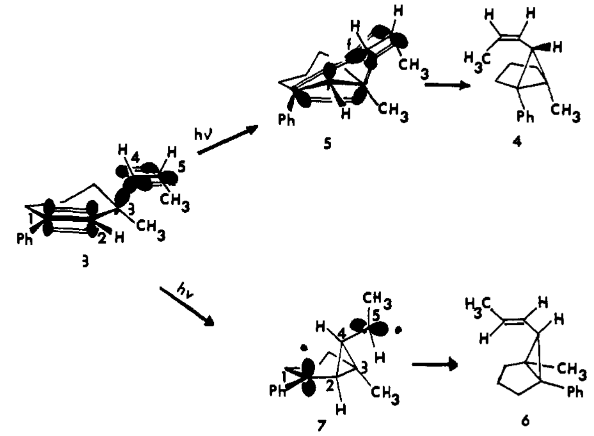
Sir:

The photochemical di-π-methane rearrangement continues to attract a great deal of attention due to both its general nature and interesting mechanistic variations. Of prime interest to us has been the stereochemistry of this excited-state atom reorganization process which converts di-π-methane systems (**1**) to π-substituted cyclopropane products (**2**). Our previous investigations[2] of the photochemistry of 1-phenyl-3-methyl-3-(1-*cis*-propenyl)cyclohexene (**3**) have indicated that the conversion of 1,4-dienes to vinylcyclopropanes by this pathway proceeds with remarkable stereospecificity, accountable for on the basis of a concerted di-π-methane rearrangement with preferential three-ring formation by disrotatory motion of the orbitals at C-1 and C-3 anti to the migrating propenyl group.

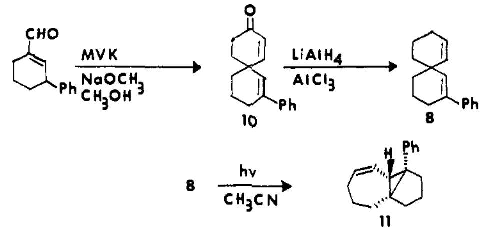


Thus, our rationale for formation of 1-phenyl-5-methyl-*endo*-6-(1-*cis*-propenyl)bicyclo[3.1.0]hexane (**4**) from the singlet excited state of **3** was based on a concerted pathway which proceeded through the low-energy anti-disrotatory transition-state orbital geometry **5**. Similarly, our explanation for formation of the endo trans propenyl product **6** was based on a nonconcerted pathway in which diradical **7** was preferentially converted to product by backside displacement of C-4 by C-1 at C-3, as shown in Scheme I. Other observations on the singlet[3] and triplet[4] di-π-methane reactivity have further verified our conclusions. We have continued our initial studies of these intriguing aspects of the di-π-methane rearrangement stereochemistry with the hope of gaining more insight into the nature of the factors which control this stereoselectivity and now report our results on the photochemistry of a structurally rigid 1,4-diene, 2-phenylspiro[5.5]undeca-1,7-diene (**8**), which rearranges efficiently on direct irradiation with syn-disrotatory three-ring formation.

Scheme I



Preparation of **8** was by the sequence involving methyl vinyl ketone annelation of the known[2] 3-phenylcyclohexene-1-carboxaldehyde (**9**) followed by lithium aluminum hydride–aluminum chloride reduction of the formed 8-phenylspiro[5.5]undeca-1,7-dien-3-one (**10**).



Irradiation[5] of **8** gave 11-phenyltricyclo[5.4.0.0^{7,11}]undec-2-ene (**11**). The structure of photoproduct **11**

---

[1] A preliminary report of this work was presented at the 165th National Meeting of the American Chemical Society, Dallas, Texas, 1973. Abstract of Papers No. Orgn-87.

[2] P. S. Mariano and J. K. Ko, *J. Amer. Chem. Soc.*, **94**, 1766 (1972); *ibid.*, in press.

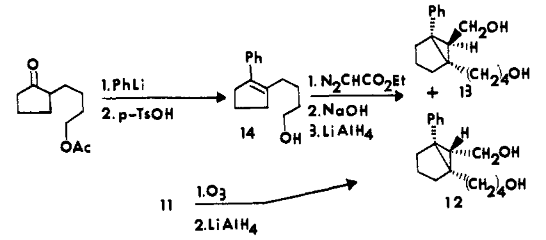
[3] H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. W. Kurtz, *ibid.*, **94**, 5504 (1972).

[4] J. S. Swenton, A. R. Crumrine, and T. J. Walker, *ibid.*, **92**, 1411 (1970); H. E. Zimmerman and G. Epling, *ibid.*, **92**, 1411 (1970).

[5] Irradiations were carried out in acetonitrile using a 450-W immersion lamp and a vycor or corex filter on an *ca.* 1×10^{-3} *M* solution of **8**. The photoproduct was separated conveniently from starting material using glc on a 7 ft × 0.25 in. 5% SE-30 column. Yields were *ca.* 95% at *ca.* 40–60% conversion, based on recovered starting material.

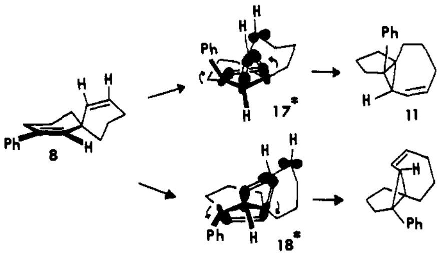
was consistent with its spectral and analytical data and was unambiguously determined by the degradation and synthetic sequence outlined in Scheme II.[6] Ozonolysis of **11** followed by reductive work-up with lithium aluminum hydride gave one of the two diols, **12**, independently prepared by the thermal reaction of ethyl diazoacetate and 4-(2-phenyl-1-cyclopentyl)butylacetate (**14**) followed by saponification and reduction. The photoproduct stereochemistry was indirectly inferred from the stereochemistry of diol **12**, which was shown to be the exo 6-hydroxymethyl isomer. In the nmr, **12** displayed a complex hydroxymethylene pattern accountable for on the basis of the exo disposition of the 6-hydroxymethyl group when compared with the patterns displayed by the analogous protons in the nmr of the model alcohols, *endo*- and *exo*-1-phenyl-5-methyl-6-hydroxymethylbicyclo[3.1.0]hexane, **15** and **16**, respectively.[7] These patterns are depicted in Figure 1.

Scheme II



Sensitized photolysis of spirodiene **8**, using benzophenone and acetophenone under conditions in which energy transfer was noted,[9] failed to produce detectable amounts of products.

Several aspects of the above observations are of interest. First, the singlet di-π-methane atom reorganization of spirodiene (**8**) appears to proceed through the syn-disrotatory transition-state orbital geometry **17**‡, as is required by the rigid structural constraint placed on the 1,4-diene chromophore rendering the anti-disrotatory reaction mode through **18**‡ of higher energy. In energy terms, the anti-disrotatory reaction pathway, exclusively followed by other 1,4-diene systems,[2,3] must represent only a slight preference over its syn counterpart and most certainly not a requirement for the di-π-methane rearrangement; *i.e.*, the energy differences between the two electronically allowed[10] disrotatory transition-state orbital geometries must be small in order for structural perturbations which prohibit the lower energy stereochemistry not to have drastic effects on the efficiency of the reaction.



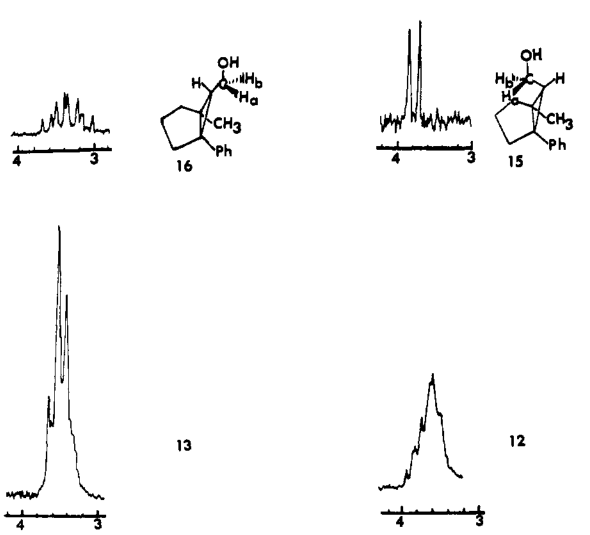


Figure 1. The hydroxymethylene proton region of the nmr of the model alcohols **15** and **16** and the diols **12** and **13** demonstrating the effects of environment on the magnetic nonequivalence of the diastereotopic methylene protons.

Our results seem to indicate that the nature of this small stereochemical driving force in the di-π-methane rearrangement of acyclic and nonconstrained cyclic 1,4-dienes might lie in the initial orientation of interacting orbitals or in least motion of the orbital at C-3 during the initial phases of rearrangement. Thus, in the absence of structural constraints, the preference for anti-disrotatory three-ring formation is apparently a consequence of the better initial overlap of the back lobe at C-3 with the p orbital at C-1 and of less motion of C-3 during inversion than retention of configuration.

It is also interesting that the general structural–multiplicity relationships noted earlier[11] for the di-π-methane rearrangement have exceptions. In particular, the spirodiene **8** is incapable of free-rotor[10,12] deactivation and is unreactive from its triplet excited state.

More of the interesting features of the di-π-methane rearrangement are continuing to surface. Thus, this ubiquitous excited-state atom reorganization process continues to warrant our further investigations.

Acknowledgment. Support of this research by the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Robert A. Welch Foundation is gratefully acknowledged.

Patrick S. Mariano,* Richard B. Steitle
Department of Chemistry, Texas A&M University
College Station, Texas 77843

Received June 25, 1973

---

(6) All new compounds gave satisfactory analytical and spectral data.

(7) The diastereotopic hydroxymethylene protons in the model alcohols **15** and **16** display strikingly different patterns in the nmr. In the exo isomer, **16**, these protons are magnetically nonequivalent and thus appear as the expected AA′M pattern. However, in the endo isomer, **15**, they are magnetically equivalent and, thus, appear as a simple A_2M doublet.[2,8] In the nmr spectra of the diols **12** and **13**, superimposed on these signals are the triplets for the side-chain hydroxymethylene protons.

(8) P. S. Mariano and R. McElroy, *Tetrahedron Lett.*, 5305 (1972).

(9) Energy transfer in the benzophenone sensitized photolysis was proven by observation that spirodiene **8** quenched the well-known triplet photoreduction of benzophenone with benzhydrol.

(10) The two disrotatory transition-state orbital geometries are isoconjugate with Möbius benzene and, therefore, expected to be of low energy (allowed) in the excited state manifold: H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971).

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

(12) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6259 (1970).