"important" to the molecular structure: $-COCH_3$, $-OCH_3$, $-OSO_2CH_3$, $-COH$, $-NCOCH_3$, $-OCOPh$, etc.

At high S_t/E_t, where $S \approx S_t$, the approximation $K \approx (E_t - E)/S_tE$ was used to obtain eq 2. Plots of

$$(\Delta_{\text{obsd}}{}^{i})^{-1} = (\Delta_{\text{max}}{}^{i}E_t)^{-1}S_t + (\Delta_{\text{max}}{}^{i}E_tK)^{-1} \qquad (2)$$

$1/\Delta_{\text{obsd}}$ *vs.* S_t give straight lines (Figure 1) from which the slopes and intercepts give $\Delta_{\text{max}}{}^{i}$ and K. The K values at ambient probe temperature (32 ± 1°) for isopropyl alcohol, tetrahydrofuran, 2-butanone, isopropenyl acetate, and allyl acetate are 97 ± 8, 57 ± 3, 32 ± 3, 27 ± 3, and 26 ± 3 l. mol^{-1}, respectively. The relative ordering is consistent with that estimated qualitatively by competition experiments.[6] The calculated $\Delta_{\text{max}}{}^{i}$ are consistent with the $\Delta_{\text{max}}{}^{i}/\Delta_{\text{max}}{}^{j}$ slopes, *e.g.*, Δ_{max} for the 2- and 3-methylenes of tetrahydrofuran are calculated to be 1948 and 793 Hz; ratio 2.46. The plot of $\Delta_{\text{obsd}}{}^{2\text{-H}}$ *vs.* $\Delta_{\text{obsd}}{}^{3\text{-H}}$ gives slope 2.40.

This analysis allows convenient estimations of Δ_{max} and K.[13a] Both are necessary for meaningful comparisons of vastly different substrates. The pseudocontact shift equation[1-3] (above) properly requires $\delta_{\text{max}}{}^{i}$, not some arbitrarily selected $\delta_{\text{obsd}}{}^{i}$.

Acknowledgment. The author thanks Professor Robert G. Bergman for his generous encouragement of this work and his commitment of partial financial support from National Institutes of Health Grant No. AM-AI-13554, and Professor John D. Roberts for his stimulating discussions and helpful suggestions.

[13a] NOTE ADDED IN PROOF. After submission of this report, a communication reported the use of S_t *vs.* $1/\Delta_{\text{obsd}}$ to calculate Δ_{max} and K for propylamine and neopentyl alcohol using the less soluble Eu(dpm)$_3$ reagent (I. Armitage, G. Dunsmore, L. D. Hall, and A. G. Marshall, *Chem. Commun.*, 1281 (1971)).

[14] National Science Foundation Predoctoral Fellow, 1968-1971.

Donald R. Kelsey[14]
Contribution No. 4352
Gates and Crellin Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91109

Received October 13, 1971

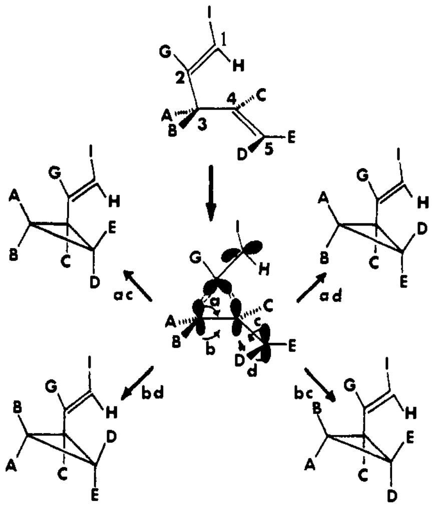
The Stereochemistry of Excited State Atom Reorganization Processes. Di-π-methane Rearrangement

Sir:

The photochemical di-π-methane rearrangement of di-π-methanes to π-cyclopropanes has become one of the more general excited state atom reorganization reactions.[1] A large effort has been directed recently at determining how structures and electronic properties of the di-π-methanes influence the direction, multiplicity, and efficiency of this process.[1,2] Another interesting, yet less studied,[3] facet of this excited state process is its stereochemistry, *i.e.*, whether the process is a concerted one and, if so, which of the manifold of transition-state orbital geometries is of lowest energy. In addition, the question of whether or not the preferred stereochemical pathways are influenced by structure and multiplicity of the di-π-methanes seems important.

Initial considerations of the stereochemistry of this process include expectations based upon the variety of possible mechanisms for the conversion of di-π-methanes to π-cyclopropanes. For example, the four concerted reaction pathways, which correspond to π migration from C-3 to C-4 in concert with C-3–C-5 disrotatory ring closure, syn (pathway ac in Chart I) or anti (bd) to the migrating moiety, or conrotatory closure with retention (ad) or inversion (bc) at C-3, lead to stereochemically distinct π-cyclopropanes, when starting with an appropriately substituted di-π-methane in which free rotation about the C-3–C-4 bond is restricted. On the other hand, nonconcerted processes are expected to display a manifold of stereochemical outcomes depending on the degree of nonsimultaneity of bond formation and cleavage. In the course of our studies, we have prepared model 1,4-dienes, having necessary substituents and structures to reflect favored pathways in the vinylcyclopropanes produced. We would like to report some of our initial results from studies on one of these, 1-phenyl-3-methyl-3-(*cis*-1-propenyl)cyclohex-1-ene (**1**),[6] which indicate that anti-disrotatory C-3–C-5 ring closure is preferred.

Chart I. Di-π-methane Concerted Pathways



Direct irradiation of **1** in hexane resulted in formation of a complex mixture from which two major products were separated. The spectral and analytical data indicated that both the major I (37.8%) and minor II (24.3%)[7] photoproducts are isomeric with the starting diene and have structures in which the propenyl group is retained and the styryl is lost, as in the propenylbicyclo[3.1.0]hexanes (**2–5**).

In order to distinguish between these possibilities, degradation of the minor direct irradiation photo-

---

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

[2] (a) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6259, 6267 (1970); (b) H. E. Zimmerman and A. Baum, *ibid.*, **93**, 3646 (1971).

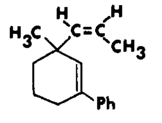
[3] The stereochemistry of the benzovinyl version of this rearrangement has been investigated by Zimmerman[4] and Swenton[5] who found pathways involving anti-dirotatory closure (path bd in Chart I) to be preferred.

[4] (a) H. E. Zimmerman and G. Samuelson, *J. Amer. Chem. Soc.*, **91** 5307 (1969); (b) H. E. Zimmerman and G. Epling, *ibid.*, **92**, 1411 (1970).

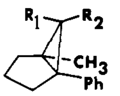
[5] J. S. Swenton, A. L. Crumrine, and T. J. Walker, *ibid.*, **92**, 1406 (1970).

[6] (a) Full details of the synthetic and degradative sequences used in this work will be given in our full paper. All new compounds gave satisfactory quantitative analyses. (b) The spectral properties (ir, absence of absorption in the 9.8–12.5-μ region) and known stereoselectivity of the Wittig reaction support the assignment of cis stereochemistry to our starting diene 1.

[7] Separation was accomplished using glc on a 12 ft × $^1/_4$ in. column of 2% SE-30 on Chromosorb P (acid washed) at 210°; yields are based on unrecovered starting material.



1



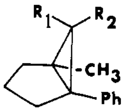
2, R_1=H; R_2=cis,-CH=CHCH$_3$

3, R_1=H; R_2=trans,-CH=CHCH$_3$

4, R_1=cis,-CH=CHCH$_3$; R_2=H

5, R_1=trans,-CH=CHCH$_3$; R_2=H

product II was carried out by a sequence involving ozonolysis, followed by sodium borohydride reduction. This afforded one of the two alcohols, **6** and **7**, prepared from the copper-catalyzed addition of ethyl diazoacetate to 1-methyl-2-phenylcyclopentene followed by saponification and lithium aluminum hydride reduction.[6a] The actual alcohol produced was found to be 1-methyl-5-phenyl-6-*endo*-hydroxymethylbicyclo[3.1.0]hexane (**6**) on the basis of the differences between the europium-induced shifts of the methyl *vs.* methylene proton resonances in **6** and its exo isomer **7**.[8] In addition, the infrared spectrum of II displayed an intense band at 10.3 μ, allowing assignment of the structure of 1-methyl-5-phenyl-6-*endo*-(*trans*-1-propenyl)bicyclo[3.1.0]hexane (**5**) to this photoproduct. When I was subjected to this same degradation sequence it also afforded the endo alcohol **6**. Thus, its structure must be that of 1-methyl-5-phenyl-6-*endo*-(*cis*-propenyl)bicyclo[3.1.0]hexane (**4**), differing from II only in configuration about the double bond.[9]

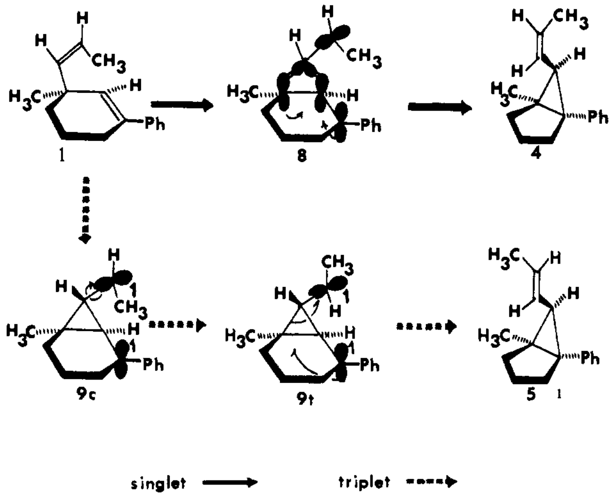


6, R_1=CH$_2$OH; R_2=H

7, R_1=H; R_2=CH$_2$OH

The photosensitized irradiation of **1** with benzophenone[10] proceeded with remarkable efficiency and gave, as the only detectable product,[11] the *endo-trans*-propenyl product **5** in near quantitative yield.[7]

In the di-π-methane reorganization pathway of **1**, a preference for disrotatory ring closure between C-3 and C-5 anti to the migrating propenyl group exists, independent of excited state multiplicity, as demonstrated by the exclusive formation of the *endo*-propenyl products, **5** and **4**, from the triplet and singlet excited states of diene **1**, respectively.[12] These results can best be explained in terms of two mechanisms, differing only in the simultaneity of bond formation and cleavage during rearrangement. A totally concerted singlet mechanism, *via* the electronically and structurally allowed[13] anti-disrotatory transition-state **8**, would lead to a singlet product with correct stereochemistry, *i.e.*, **4**. The alternate concerted pathway, through the syn-disrotatory closure, of apparent equal energy,[13] is not followed.



The triplet pathway requires a mechanism in which inversion of configuration about the double bond and stereospecific anti-disrotatory ring closure occur. A mechanism that accommodates both observations involves the intermediacy of diradical **9c** in which rotation about the C-1–C-2 bond results in the transoid conformation **9t**, capable of proceeding to **5** by "backside" attack of the anti lobe at C-5 on C-3. Further studies, directed at determining the role of structure and multiplicity on the preferred stereochemical pathways in the di-π-methane rearrangement, are in progress.

Acknowledgment. Support of this research by the Petroleum Research Fund of the American Chemical Society, the Research Corporation, and the Texas A&M Research Council is gratefully acknowledged.

(8) A change in the molar ratio of Eu(fod)$_3$ to endo alcohol **6** from 0 to 0.6 resulted in a $\Delta\nu$ for the methyl resonance of 139 Hz and for the low-field methylene of 247 Hz. This is compared to the striking reversal for the exo alcohol **7** which displayed a $\Delta\nu$ for the methyl resonance of 241 Hz and for the low-field methylene of 109 Hz on changing from 0 to 0.75 molar ratio of the lanthanide. In addition, dramatic differences in the patterns displayed by the hydroxymethylene protons in **6** and **7** were observed (**6**, A$_2$X, d, J_{AX} = 7.5 Hz; **7**, ABX, dd, J_{AX} = 7.0 Hz, J_{BX} = 7.5 Hz, J_{AB} = 11.0 Hz). This is in accord with the expected differences between the magnetic environments of the diastereotopic protons in the endo and exo isomers.

(9) The absence of bands in the 9.8–12.5-μ region in the ir and the similarity of the nmr spectra of I and II (except in the olefinic region) support our structural assignments.

(10) The conditions used allowed for greater than 99% light absorption by benzophenone and efficient energy transfer to **1** from benzophenone triplet, only.

(11) That no detectable quantities of the trans isomer of **1** were observed, even in low conversion sensitized runs, is interesting and leads to the conclusion that isomerization about the propenyl double bond is slower than reaction by the di-π-methane pathway of the triplet monocyclic diene. A contrastingly different result was obtained by Zimmerman and Pratt[2a] for an acyclic 1,4-diene system.

(12) (a) For the direct irradiation reaction, the assumption is made that the trans product **5** results from the triplet of **1**, itself formed by intersystem crossing from its sluggishly reacting singlet excited state. Quenching studies are now in progress to determine if this is the case. (b) Another explanation for the exclusive formation of trans product **5** in the sensitized irradiation, which involves preliminary isomerization of **1**, *via* its triplet, to either (1) *trans*-**1** exclusively, followed by reaction in which the configuration about the double bond is retained, or (2) a mixture of *cis*- and *trans*-**1** in which trans reacts much more rapidly, can be ruled out on the basis of our varying conversion runs.[11]

(13) Both the syn and anti disrotatory transition states are isoconjugate with Möbius benzene and, therefore, are predicted to be of lowest energy (allowed) in the excited state process of **1**.[14] The two higher energy orbital arrangements, involving conrotatory closure, are also forbidden on structural grounds, since both would lead to the excessively strained trans-fused bicyclo[3.1.0]hexane ring system.

(14) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564, 1566 (1966).

Patrick S. Mariano,* Jan-kwei Ko
Department of Chemistry, Texas A&M University
College Station, Texas 77843

Received November 15, 1971

Solvent Effects on the Visible Circular Dichroism of Copper(II) Complexes with N,N-Dialkylated Amino Acids

Sir:

With the exception of L-proline, the visible circular dichroism spectra thus far reported for 2:1 complexes of amino acid anions with copper(II) in aqueous solution all