# The Di-π-methane Rearrangement. Stereochemistry[1]

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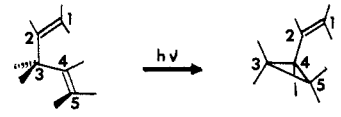
**Abstract:** The preferred stereochemical pathways in the di-π-methane rearrangement (the excited state conversion of di-π-methanes to π-cyclopropanes) have been determined, using 1-phenyl-3-methyl-3-(1-*cis*-propenyl)cyclohex-1-ene (**5**) as the model di-π-methane system. The major products of direct irradiation were determined to be 1-phenyl-5-methyl-6-*endo*-(1-*cis*-propenyl)bicyclo[3.1.0]hexane (**10**) and its 6-*endo*-*trans*-propenyl isomer (**12**) on the basis of degradation and independent synthetic sequences, having the isomeric alcohols, **18** and **19**, as key intermediates. Photosensitization and quenching studies were undertaken. A novel diagnostic method for determining when one of several products of direct irradiation reactions results from the singlet excited state of reactant is presented and applied to the conversion of **5** to **10** and **12**. Our results demonstrate that the *cis*-propenyl product, **10**, is produced exclusively from the singlet excited state of **5** and that the *trans*-propenyl isomer, **12**, results from triplet-state reactions. The presently studied di-π-methane rearrangement is contrasted from a mechanistic viewpoint with other systems and rationale to explain the stereochemistry and regiochemistry of these reactions are presented.

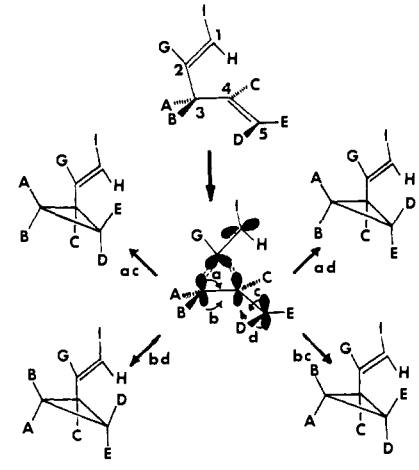
The di-π-methane rearrangement (the conversion of di-π-methane systems (**1**), having two π-moieties attached to a single $sp^3$-hybridized or saturated carbon, to π-substituted cyclopropanes (**2**)) has emerged as one of the most general of excited state molecular rearrangement processes. Recent studies have uncovered several of the intriguing aspects of this reaction with regard to its general nature,[2] regiochemistry,[3] and the apparent structure multiplicity[2,4] relationship.[5] One of the most interesting aspects of this rearrangement is its stereochemistry, due to its mechanistic implications and importance in synthetic applications.




**1** **2**

Our initial studies[6] were aimed at determining the favored stereochemical pathways by which di-π-methanes rearrange to their corresponding π-cyclopropanes and their relationship to the mechanism of this versatile excited-state process. In order to design systems which are capable of demonstrating favored stereochemical pathways simply on the basis of the products formed and their stereochemistry, it was first necessary to consider the possible mechanisms responsible for conversion of di-π-methanes to π-cyclopropanes. For example, a concerted process has, *a priori*, eight possible stereochemical outcomes as a result of the relative configurations about the carbon–carbon double bond in the migrating π moiety (C-1–C-2) and cyclopropane ring carbons (C-3, C-4, and C-5). Four of these possibilities, shown in Chart I, correspond to

**Chart I.** Four Possible Concerted Pathways for the Conversion of Di-π-methanes to π-Cyclopropanes




suprafacial π migration from C-3 to C-4 in concert with disrotatory ring formation between C-3 and C-5 either syn (pathway ac) or anti (pathway bd) to the migrating group, or conrotatory closure with retention (pathway ad) or inversion (pathway bc) at C-3. Other concerted pathways are possible and predict the same possible stereochemistries in the formed cyclopropane but different configuration about the migrating π bond.

On the other hand, nonconcerted isomerization pathways, two of which are delineated in Chart II, would be expected to display a manifold of stereochemical outcomes due to the intermediacy of diradical species, like **3** and **4**, in which rotation about the free carbon–carbon bonds would randomize stereochemistry. It is evident that di-π-methane systems which contain proper substituent patterns (as shown in Charts I and II) would be capable of displaying mechanistic and stereochemical preferences in rearrangement by the nature and number

(1) Preliminary reports of the results of our present studies have appeared: (a) P. S. Mariano and J. K. Ko, *J. Amer. Chem. Soc.*, **94**, 1766 (1972); (b) P. S. Mariano, J. K. Ko, and R. B. Steittle, Manuscript of Contributed Papers, IVth IUPAC Symposium on Photochemistry, Baden-Baden, Germany, 1972, p 156.

(2) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969), and references cited therein.

(3) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6259, 6267 (1970).

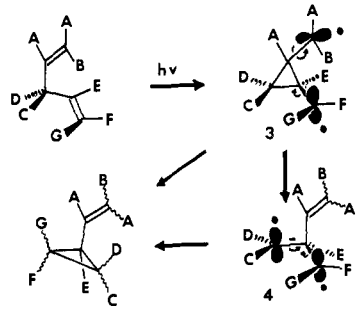
(4) H. E. Zimmerman and G. A. Epling, *ibid.*, **92**, 1411 (1970); J. S. Swenton, A. R. Crumrine, and T. J. Walker, *ibid.*, **92**, 1406 (1970).

(5) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, 73, 531 (1973), for a general review of the most interesting aspects of the di-π-methane process.

(6) Prior studies by Zimmerman and Pratt[3] had demonstrated that the di-π-methane rearrangement of acyclic 1,4-dienes proceeds with retention of configuration about the migrating π bond. In addition, subsequent to our initial investigation[1] Zimmerman and coworkers[7] have shown that bonding between C-3 and C-4 in cyclopropane formation prefers use of the anti-lobe at C-5 or that motion d in Chart I predominates.

(7) H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. W. Kurtz, *J. Amer. Chem. Soc.*, **94**, 5504 (1972).

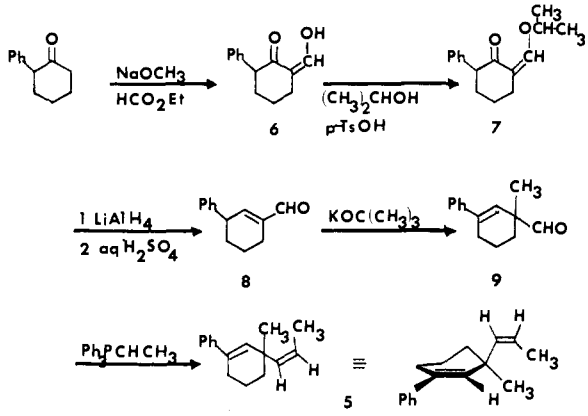
**Chart II.** Nonconcerted Di-$\pi$-methane Pathways



of $\pi$-substituted cyclopropane products produced. Ideal for this purpose and, therefore, chosen for our initial investigation was 1-phenyl-3-methyl-3-(1-*cis*-propenyl)cyclohexene (**5**), whose synthesis and photochemistry we are presently describing.

**Preparation of 1-Phenyl-3-methyl-3-(1-*cis*-propenyl)-cyclohexene.** The synthetic design chosen for the preparation of di-$\pi$-methane **5** followed the well-known sequence for conversion of $\beta$-dicarbonyl compounds to their corresponding $\alpha,\beta$-unsaturated carbonyl analogs.[8] Accordingly, the known[9] 2-phenylcyclohexanone was formylated using known conditions with sodium methoxide and ethyl formate yielding 2-phenyl-6-formylcyclohexanone (**6**), which was converted to its *O*-isopropyl ether, **7**. Lithium aluminum hydride reduction of **7** followed by aqueous acid hydrolytic work-up gave the requisite 3-phenylcyclohexene-1-carboxaldehyde (**8**) which was conveniently converted to **9** by methylation and then to **5** by a Wittig reaction with ethylidene triphenylphosphorane. This synthetic sequence is outlined in Chart III.

**Chart III.** Synthetic Pathway for Preparation of 1-Phenyl-3-methyl-3-(1-*cis*-propenyl)cyclohexene (**5**)



The structure and stereochemical[10] assignment to the *cis*-phenylpropenylcyclohexene **5** (>95% *cis*-propenyl) were confidently made on the basis of the synthetic pathway used for its preparation and confirmed by its nmr, infrared, and ultraviolet spectra (see Experimental Section).

(8) W. F. Gannon and H. O. House, *Org. Syn.*, **40**, 14 (1960) (1953); M. Stiles and A. Longroy, *Tetrahedron Lett.*, 337 (1961).

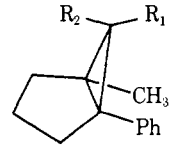
(9) C. C. Price and J. V. Karabinos, *J. Amer. Chem. Soc.*, **62**, 1159 (1940).

(10) The assignment of cis stereochemistry about the propenyl double bond was made partially on the basis of the known stereochemical course of the Wittig reaction[11] and by its infrared which displayed no band in the 9.6–12.5 $\mu$ region.[12]

(11) J. Reucroft and P. G. Sammes, *Quart. Rev., Chem. Soc.*, **25**, 135 (1971), and references cited therein.

(12) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 25.

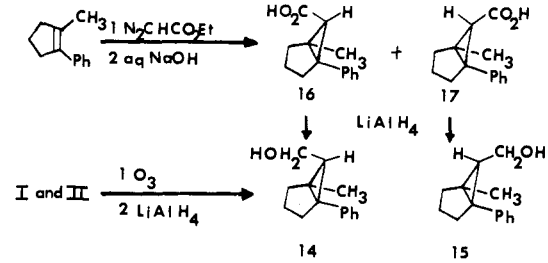
**Direct Irradiation Studies of 5.** Direct irradiation of 1-phenyl-3-methyl-3-(1-*cis*-propenyl)cyclohexene (**5**) in hexane, cyclohexane, or acetonitrile, using Vycor or Corex filtered light, in a preparative apparatus afforded two major photoproducts in the following ratio: photoproducts I (37.8%) and II (24.3%) (see Experimental Section for a representative run). The analytical and spectral data of I (nmr with five aromatic hydrogens at $\tau$ 2.65, methyl singlet at 9.00, an allylic methyl doublet at 8.28, and a two vinyl hydrogen multiplet at 4.25; ir which displayed the absence of bands in the 9.6–12.5-$\mu$ region;[12] and uv which showed an absorption band characteristic of substituted phenyl, $\lambda_{max}$ 258 nm ($\epsilon$ 870)) indicated that it was isomeric with the starting diene, **5**, and had a structure in which the *cis*-propenyl group is retained and the styryl chromophore lost. Similarly, the analytical and spectral data of II, with the exception of a strong ir band at 9.75 $\mu$, indicated that it was a *trans*-propenyl species, closely related in structure to I. On the basis of this evidence and the known course of the di-$\pi$-methane reaction, the structural candidates for the major and minor photoproducts, I and II, were deemed to be the 1-phenyl-5-methyl-6-(1-propenyl)bicyclo[3.1.0]hexanes, **10–11** and **12–13**, respectively.



**10**, $R_1$ = H; $R_2$ = *cis*-CH=CHCH$_3$
**11**, $R_1$ = *cis*-CH=CHCH$_3$; $R_2$ = H
**12**, $R_1$ = H; $R_2$ = *trans*-CH=CHCH$_3$
**13**, $R_1$ = *trans*-CH=CHCH$_3$; $R_2$ = H

**Photoproducts Structure Proofs.** In order to distinguish between these possibilities for the structures of I and II, unambiguous structure proofs were undertaken and obtained by the sequences outlined in Chart IV.

**Chart IV.** Degradation and Independent Synthetic Sequences for Proof of Structures of I and II



Photoproduct I, when subjected to ozonolysis followed by exhaustive reductive work-up with either lithium aluminum hydride or sodium borohydride, afforded only one (**14**) of the two alcohols, *endo*- and *exo*-1-phenyl-5-methyl-6-hydroxymethylbicyclo[3.1.0]hexane (**14** and **15**). These were independently prepared by the copper-catalyzed addition of ethyl diazoacetate to 1-methyl-2-phenylcyclopentene followed by saponification to the *endo*- and *exo*-bicyclic carboxylic acids, **16** and **17**, chromatographic separation, and independent reduction with lithium aluminum hydride. When photoproduct II was subjected to ozonolysis followed by reductive work-up, it also yielded **14**.

The stereochemistry at carbon-6 in the synthesized

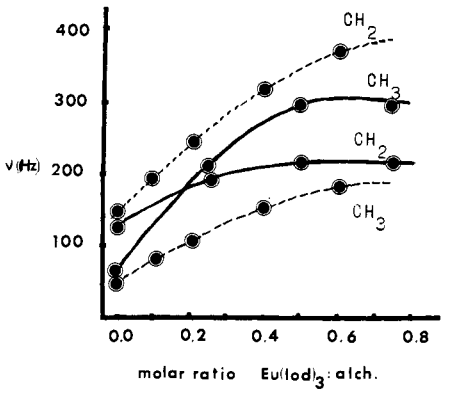
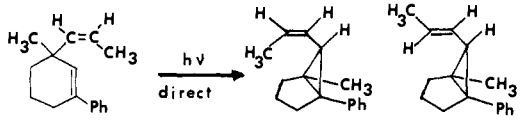



Figure 1. Europium-induced shifts of methyl ($CH_3$) and low-field methylene ($CH_2$) proton resonances in *endo*- (- - -) and *exo*-1-phenyl-5-methyl-6-hydroxymethylbicyclo[3.1.0]hexane (—).

alcohols and, thus, in the alcohol obtained from degradation of photoproducts I and II was conveniently determined using nmr spectroscopy in conjunction with the lanthanide shift reagent, trisperfluorobutylpivaloylmethanatoeuropium ($Eu(fod)_3$). As shown in Figure 1, the methyl resonance in alcohol **15** displays a marked shift to low field upon addition of increasing molar quantities of $Eu(fod)_3$ in comparison to the methyl resonance in **14** and, in addition, the low-field cyclopentano methylene resonances in **14** display a larger low-field shift than those in **15** on increasing $Eu(fod)_3$ concentrations. These observations are in accord with assignment of the *endo*-hydroxymethyl stereochemistry to alcohol **14**, the one produced on ozonolytic and reductive degradation of photoproducts I and II.

Thus, on the basis of the spectral and analytical data, together with the degradative and synthetic information, the structures of the major and minor direct irradiation photoproducts can be assigned as I, 1-phenyl-5-methyl-6-*endo*-(1-*cis*-propenyl)bicyclo[3.1.0]hexane (**10**), and II, its *trans*-propenyl isomer, **12**.




5 10 11

**Reaction Multiplicity Studies.** Having established the structures of the major and minor photoproducts obtained upon direct irradiation of **5**, we initiated studies directed at determining the mechanisms of the excited-state transformation observed. Specifically, the excited-state multiplicities of **5** responsible for production of **10** and **12** were investigated.

The photosensitized irradiation of 1-phenyl-3-methyl-3-(1-*cis*-propenyl)hexene (**5**) with benzophenone, under conditions which allowed for >99% of the light to be absorbed by the sensitizer and which maximized triplet energy transfer, proceeded smoothly and produced the *endo-trans*-propenyl product **12** in near quantitative yield **13**.[13]

In an attempt to determine whether the endo-*trans*-propenyl photoproduct (**12**) results exclusively from

(13) No detectable quantities of the trans isomer of **5** were observed, even at low conversions. The photochemical fate of products **10** or **12** has not been determined. At conversions between 10 and 40% in the sensitized reaction, **12** and **5** were the only materials detected.

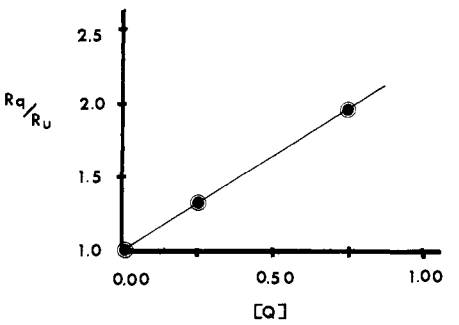



Figure 2. Plot of ratio of quenched to unquenched product **10**:**12** ratios *vs.* 2,5-dimethyl-2,4-hexadiene concentrations (*M*).

triplet excited state reaction pathways in the direct irradiation reaction or if it is one of two singlet products, quenching studies using 2,5-dimethyl-2,4-hexadiene as triplet quencher were undertaken. A rather simple and diagnostic method, used to distinguish between the alternate pathways for the production of **12** (*i.e.*, singlet and triplet) in the direct irradiation reaction, was employed. This method derived from the standard Stern–Volmer treatment of triplet excited state reactions (see Appendix) and is based on the fact that yields of singlet products will be unaffected by the presence of known triplet quenchers. In general, when two products of direct photolysis result from reaction of the singlet and triplet excited states of reactant, respectively, then the ratio of the quenched to the unquenched product ratios should vary linearly with quencher concentration, according to eq 1, in which $k_q$ is the rate constant for bimolecular quenching, $k_{dt}$ the rate constant for nonreactive triplet deactivation, and $k_3$ the rate constant for production of the triplet product (see Appendix). It should be mentioned that this method also avoids possible complications due to singlet quenching

$$\frac{R_q}{R_u} = 1 + \frac{k_q}{k_{dt} + k_3}[Q] \qquad (1)$$

when higher than normal triplet quencher concentrations are required. In essence, the quantity of singlet product serves as an internal standard, relative to which the quantity of triplet product should decrease on addition of quencher.

The results of the application of this method to the direct irradiation of the diene **5** are given in Table I and

**Table I.** Results of Quenched Photolyses of 1-Phenyl-3-methyl-3-(1-*cis*-propenyl)hexene (**5**) with 2,5-Dimethyl-2,4-hexadiene

| Concn[a] of 2,5-dimethyl-2,4-hexadiene, *M* | Ratio of **10**:**12** ($R_u$ and $R_q$) | Ratio of quenched to unquenched **10**:**12** ratio ($R_q/R_u$) |
|---|---|---|
| 0.00 | 1.55 | |
| 0.00 | 1.71 | 1.00[b] |
| 0.00 | 1.62 | |
| 0.25 | 2.21 | 1.36 |
| 0.75 | 3.21 | 1.97 |

[a] Concentrations of diene **5** were $1.57 \times 10^{-2}$ *M* in cyclohexane. [b] Average of $R_u$'s from runs 1–3 used.

summarized in Figure 2. The decrease in the relative amounts of the endo-trans photoproduct, **12**, formed on

increasing concentrations of 2,5-dimethyl-2,4-hexadiene[14] and the near linearity of the $R_q/R_u$ *vs.* quencher concentration plot suggest that the singlet excited state of **5** rearranges exclusively to the *endo-cis*-propenyl product, **10**, and that the *trans*-propenyl isomer, **12**, results from triplet reaction pathways in the direct irradiation reaction.

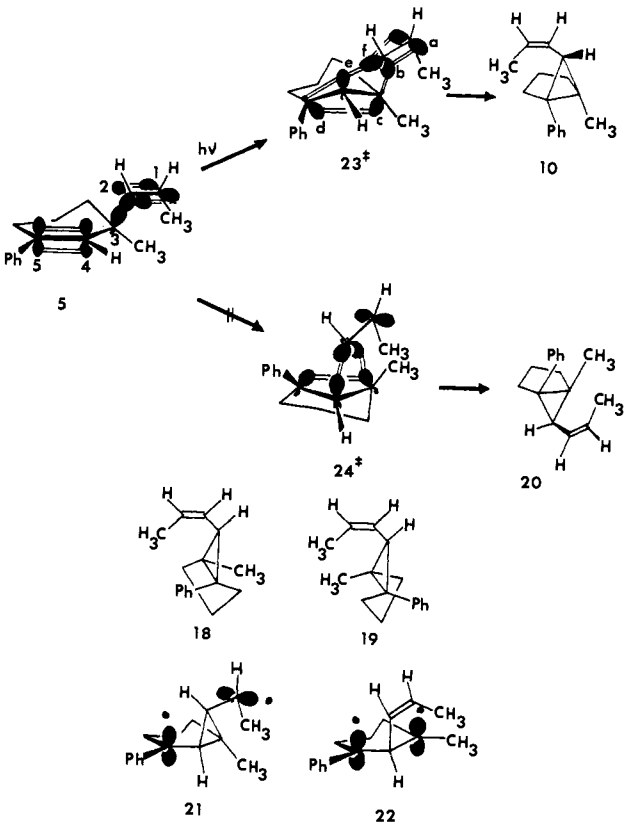
## Discussion

**Di-π-methane Stereochemistry.** Our observations indicate that the di-π-methane rearrangement of the singlet excited state of 1-phenyl-3-methyl-3-(1-*cis*-propenyl)hexene (**5**) proceeds with stereospecificity in both π migration and cyclopropane ring formation. In this conversion the configurational integrity about the π bond in the migrating propenyl moiety is maintained and cyclopropane ring formation between C-3 and C-5 during rearrangement must occur exclusively with disrotatory overlap of the orbitals involved, anti (or trans) to the migrating propenyl group.[15] This analysis of the stereochemical outcome of the singlet reaction of **5** is based simply on the fact that products expected from the other formalistic modes of π migration or cyclopropane formation, like the highly strained trans-fused bicyclic hexanes, **18** and **19**, the *exo-cis*-propenyl product **20**, *etc.*, are not formed upon direct irradiation of **5** (Scheme I).

Reaction mechanisms consistent with stereospecific π migration and cyclopropane formation for the singlet conversion of **5** can be postulated. It is first necessary to exclude from consideration any which require the intermediacy of long-lived cyclopropyldicarbinyl diradicals, like **21** and **22**, in which stereochemistry might be lost about the C-1–C-2 bond or from which nonspecific cyclopropane formation is possible. The most logical rationale which most easily explains the observed stereospecificity is in terms of a concerted mechanism *via* the transition state orbital geometry $\mathbf{23}^{\mp}$ in which orbital overlap, according to the cycle -a-b-c-d-e-f-, corresponds to what we have termed[15] anti-disrotatory cyclopropane formation simultaneous with propenyl migration. Concerted pathways proceeding through analogous transition state orbital geometries have been used before in describing the di-π-methane rearrangement.[2-4,7] It is interesting that our stereochemical results offer firm confirmation of these earlier predictions which were based upon orbital symmetry or transition-state π-electron considerations.

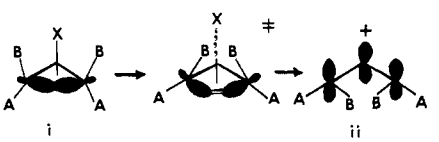
It does not appear that the preference for the anti-disrotatory transition-state orbital geometry, $\mathbf{23}^{\mp}$, results solely from π-electron or orbital symmetry factors, since both the anti- and syn-disrotatory ($\mathbf{24}^{\mp}$) orbital arrangements are expected to have equal π-energy contents or symmetry allowedness on the basis of first-order reasoning.[17] The nature of the anti- over syn-disrotatory selectivity is not totally clear but must derive from either small or large energy differences between $\mathbf{23}^{\mp}$ and $\mathbf{24}^{\mp}$ due to steric repulsion or orbital overlap. For instance, in the syn-disrotatory transition state the migrating propenyl group is entering an environment exo to the developing cyclopentano moiety and endo to the C-5 phenyl and C-3 methyl substituents.[20] The opposite relative orientation of propenyl

**Scheme I**



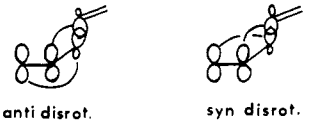

(14) At 2,5-dimethyl-2,4-hexadiene concentrations of <1.0 *M*, greater than 99% of the light above the Corex glass cut off is being absorbed by the diene **5**. However, the quenching studies are independent of this, since the results obtained depend merely on the relative amounts of products **10** and **12** formed.

(15) We suggest that the syn- and anti-disrotatory terminology be used in describing orbital overlap during cyclization or the retro processes which involve concurrent attack or departure of groups as in cyclopropane formation in the di-π-methane rearrangement or in cyclopropyl halide (i) to allyl cation (ii) conversions.[16]




(16) See, for instance, C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968).

(17) Both the syn- and anti-disrotatory transition orbital geometries are isoconjugate with Mobius benzene and, therefore, are predicted to be of lowest energy or allowed in the excited state conversion of **5** to its corresponding products.[18] An alternative method[19] having the same basic foundation for predicting the allowedness of pericyclic processes as first proposed by Zimmerman[18] would consider the anti-disrotatory pathway as a $\sigma 2_a + \pi 2_a$ change (trans addition of the C-2–C-3 σ bond trans to the C-3–C-5 π bond) and the syn-disrotatory pathway as a $\sigma 2_s + \pi 2_s$ change (cis addition of the σ bond cis to the π bond). Both are predicted to be low energy excited state pathways. The two conrotatory orbital arrangements are predicted using these π-electron treatments to be of high energy (forbidden) and should also have high energy contents due to their progression to the highly strained trans-fused bicyclics **18** and **19**.




(18) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564, 1566 (1966); *Accounts Chem. Res.*, **4**, 272 (1971).

(19) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

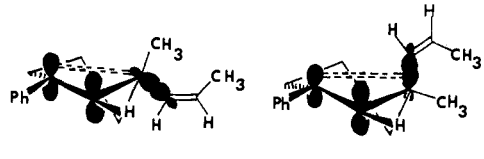
(20) Evidence is available[21] which demonstrates the need for C-3 alkyl substituents for an efficient di-π-methane process in acyclic systems. However, this does not appear to have any bearing on the possible effect of these alkyl substituents in controlling stereochemistry.

(21) H. E. Zimmerman and J. A. Pincock, *J. Amer. Chem. Soc.*, **94**, 6208 (1972); E. Block and H. W. Orf, *ibid.*, **94**, 8438 (1972).

group with ring and substituents is developing in transition state $23^{\mp}$. However, difficulties arise in attempting to utilize these differences in explaining the observed relative energies between $23^{\mp}$ and $24^{\mp}$, since it necessitates an evaluation of the steric differences between the developing cyclopentano-moiety and the phenyl and methyl substituents. On the basis of possibly naive model inspection, it would appear that these steric differences would favor the syn-disrotatory pathway and thus lead to an erroneous prediction.

Another important difference between these two stereochemically distinct pathways having the respective transition states, $23^{\mp}$ and $24^{\mp}$, lies in the configurational integrity at C-3. In the anti-disrotatory mode a net inversion of configuration at C-3 results while in the syn counterpart C-3's configuration is retained. More explicitly, the lobe of the orbital at C-3 used for bonding with C-5 differs in the syn- and anti-disrotatory pathways. Possibly, the observed preference for $23^{\mp}$ over $24^{\mp}$ is a result of the orbital overlap or motion incurred in these competing pathways or, as has been invoked to explain stereochemical results in other systems,[22] of ground-state conformation control of reacting orbital overlap. Inspection of both the ground state and anti- and syn-disrotatory excited state transition state orbital arrangements indicates that the anti pathway, from the pseudoequatorial propenyl conformation, **5e**, would involve less motion of the orbital at C-3 in bonding with C-5 than in the syn pathway, from the pseudoaxial or equatorial propenyl conformers (**5a** and **5e**). In other words the preference for the anti-disrotatory pathway might derive from the fact that it involves less changes in nuclear and electronic coordinates in reaching the point at which good orbital overlap between C-3 and C-5 is obtained or that there is better initial overlap of the orbital at C-5 with the back lobe at C-3.

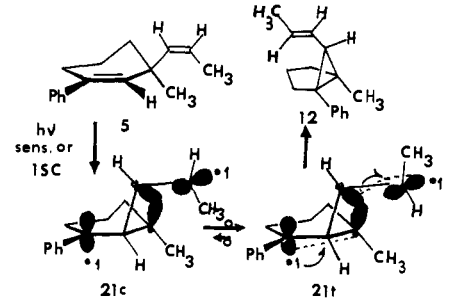
Thus, the preference for the anti-disrotatory pathway for the di-$\pi$-methane conversion of **5** *via* transition state $23^{\mp}$ might reflect orbital symmetry control in its disrotatory nature and initial orbital overlap in its anti nature. It is noteworthy that, independent of its source, the stereochemical control results in a stereospecific singlet conversion of di-$\pi$-methanes to their corresponding $\pi$-substituted cyclopropanes and add yet another intriguing observation to those made on this general rearrangement.[3,7]




5e 5a

**Triplet Reaction Stereochemistry.** The observation of exclusive formation of 1-phenyl-5-methyl-6-*endo*-(1-*trans*-propenyl)bicyclo[3.1.0]hexane (**12**) from triplet reaction pathways has two possible explanations and one interesting conclusion. It is significant that the triplet di-$\pi$-methane reaction also proceeds with stereospecific three-membered ring formation in, formally, an anti-disrotatory manner as demonstrated by the endo configuration of the 6-propenyl group in the sole triplet product. Additionally, the stereochemistry about the migrating $\pi$ bond is changed in the triplet di-$\pi$-methane reaction of **5**, a possible result of the reaction mechanism rather than simple cis–trans isomerization of the starting cis diene or vinylcyclopropane products (*vide infra*).

One mechanistic rationalization for this observation and those on related systems (*vide infra*) is in terms of a nonconcerted two-step reaction mechanism *via* the intermediate cyclopropyldicarbinyl diradical **21** in which selective conversion of the trans-bisected conformer, **21t**, to the photoproduct **12** is a result of attack by the anti-lobe at C-5 and, formally, inversion of configuration at C-3, as depicted below. The preference for inversion rather than retention of configuration at C-3 in the collapse of diradical **21** might here again be due to good initial overlap between the back-lobe at C-3 with the anti-lobe at C-5 or simple inversion at C-3 in




21c 21t

the radical displacement of C-2 by C-5. The trans conformation of **21** would appear to be of lowest energy, since in the bisected form it would minimize the steric repulsion between the C-1 methyl and C-3 methyl groups or the ring.[23] Thus, the lowest energy pathway for collapse of **21** to the vinylcyclopropane product would pass through a transition state resembling **21t** rather than **21c**, since good C-1–C-2 orbital overlap would be prevented in the latter by this steric repulsion.

This two-step mechanism finds support in several literature observations. Pitts and Hess[26] have presented evidence which indicates that triplet cyclopropyldicarbinyl diradicals, **25**, formed upon mercury-sensitized photolysis of bicyclo[3.1.0]hexan-3-one (**26**), collapse to their corresponding vinylcyclopropanes. In addition, the conversion of 5,5-diphenyl-1,3-cyclohexadiene (**27**) to, predominantly, the *trans*-diphenylbicyclohexene, **28**,[27a] and the preferential formation of the *endo*-acetylbicyclo[2.1.0]hexane, **29**, from the corresponding acetylcyclopentene, **30**,[27b] are triplet examples of the di-$\pi$-methane and oxa-di-$\pi$-methane rearrangement which display stereoselectivities in cyclopropane formation explainable on the basis of a diradical mechanism like the one presented. One point, however, that is not clarified by this mechanism is the absence of detectable quantities of the trans isomer of **5** in either the sensitized or direct irradiation reaction mixtures,[13] since cyclopropyldicarbinyl diradicals nor-

(22) W. G. Dauben, J. Rabinowitz, N. D. Vietmeyer, and P. H. Wendschuh, *J. Amer. Chem. Soc.*, **94**, 485 (1972); C. W. Spangler, Abstracts of Contributed Papers, IVth IUPAC Symposium on Photochemistry, Baden-Baden, Germany, 1972.

(23) That cyclopropyl radicals exist predominantly in their bisected conformation has been adequately demonstrated by experiment[24] and theory.[25]

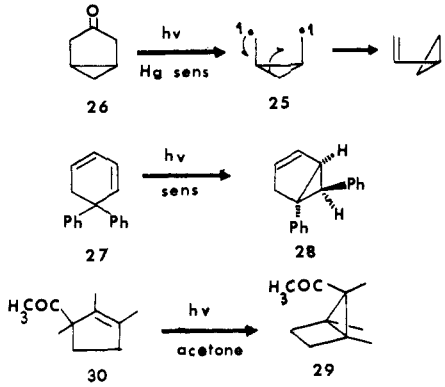
(24) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Amer. Chem. Soc.*, **91**, 1876 (1969).

(25) W. C. Danen, *ibid.*, **94**, 4835 (1972).

(26) L. D. Hess and J. N. Pitts, *ibid.*, **89**, 1973 (1967).

(27) (a) J. S. Swenton, A. R. Crumrine, and T. J. Walker, *ibid.*, **92**, 1406 (1970); H. E. Zimmerman and G. A. Epling, *ibid.*, **92**, 1411 (1970); (b) E. Baggiolini, K. Schaffner, and O. Jeger, *Chem. Commun.*, 1103 (1969).

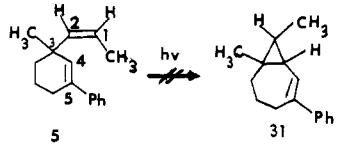
mally revert at least partially to their diene analogs. Thus, another explanation of the stereochemistry about the migrating $\pi$ bond in the triplet di-$\pi$-methane reaction of **5** might be that the process involves slow triplet cis–trans isomerization of **5** followed by rapid rearrangement of the formed trans isomer.[28]



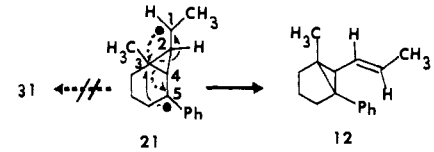

## Summary and Conclusions

The mechanistic and stereochemical results obtained from our studies of the photochemistry of 1-phenyl-3-methyl-(1-*cis*-propenyl)cyclohexene (**5**) are, in general, consistent with observations previously made on the di-$\pi$-methane reaction. For instance, the triplet excited state of **5** has those structural features which result in efficient di-$\pi$-methane to $\pi$-substituted cyclopropane conversion, due to its inability to deactivate by free rotation about the endocyclic styryl $\pi$ bond.[2] In addition, the singlet excited state of diene **5** appears to be capable of di-$\pi$-methane reaction since efficient alternative pathways, such as internal cycloaddition, are lacking.[5,29]

The regioselectivity displayed in $\pi$ migration in the singlet reaction of **5**, *i.e.*, a complete preference for migration of the less conjugated propenyl to the more conjugated styryl chromophore, parallels similar observations by Zimmerman and Pratt[3] and is readily explainable in terms of a concerted mechanism in which C-3–C-5 bonding lags slightly behind $\pi$ migration. Thus, since phenyl is more capable than methyl of stabilizing partial odd-electron character, the concerted pathway leading to **10** is expected and observed to be of lower energy than that leading to the bicyclo[5.1.0]octanes, **31**.

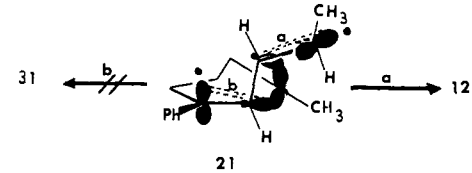



The regioselectivity observed in the triplet reaction of **5** can be accounted for using the postulated nonconcerted two-step mechanism and might result from an inequality in the degree of bond formation and cleavage in the one-step conversion of diradical **21** to the vinylcyclopropane products. If formation of the C-1–C-3 $\pi$ bond has occurred to a greater extent at the transition state than the C-3–C-5 cyclopropane bond at the transition state the odd-electron stabilizing effect of phenyl would allow conversion to **12** rather than **31** to be of lowest energy. However, it is also possible that the C-1 and C-5 orbital disposition relative to the cyclopropane ring in diradical **21** is important in regiochemical control. Close inspection of **21** reveals that the p orbital at C-1 can attain better overlap with the C-2–C-3 cyclopropane $\sigma$ bond than can the p orbital at C-5 with the C-3–C-4 cyclopropane $\sigma$ bond. Thus, the conversion of **21** to **12** might merely reflect this better alignment of




the component atomic orbitals in the breaking $\sigma$ bond and forming $\pi$ bond, as depicted below.

The most important consequence of our results lies in their demonstration of preferred stereochemical and mechanistic pathways in the general di-$\pi$-methane rearrangement. In summary, singlet excited state rearrangements of 1,4-diene prefer a concerted anti-disrotatory pathway while triplets appear to rearrange by a two-step process in which cyclopropane formation occurs in a formal anti-disrotatory manner.




## Experimental Section

**2-Phenylcyclohexanone.** This compound was prepared by the method of Price and Karakinos.[9]

**2-Phenyl-6-formylcyclohexanone (6).** The general formylation method of Johnson and coworkers[30] was used. To a solution of 27 ml of methanol in 300 ml of benzene was added 15 g (0.65 g-atom) of sodium under nitrogen at 0° and then dropwise a mixture of 25 g (0.14 mol) of 2-phenylcyclohexanone and 40 g (0.54 mol) of ethyl formate. The resulting solution was stirred overnight, ice was added cautiously until the excess sodium disappeared, and the benzene layer was separated and washed with 10% sodium hydroxide. The aqueous layers were combined, washed with ether, acidified with concentrated hydrochloric acid, and extracted with chloroform. The chloroform extracts were then washed with water, dried, and concentrated *in vacuo* giving 18.5 g (65%) of a slightly yellow oil characterized as 2-phenyl-6-formylcyclohexanone. The spectral data of this compound are the following: nmr ($CDCl_3$) $\tau$ −4.10 (br s, 1 H, OH), 1.10 (s, 1 H, CH=O), 2.50 (s, 5 H, aromatic), 6.20 (m, 1 H, PhCH), 7.40–8.30 (m, 6 H, $CH_2$); ir ($CHCl_3$) 3.30, 3.42, 3.51, 6.25, 7.50, 8.20, 8.45, 9.35, 9.70, 13.30, and 14.30 $\mu$.

**2-Phenyl-6-isopropoxymethylenecyclohexanone (7).** A solution of 32.5 g (0.16 mol) of 2-phenyl-6-formylcyclohexanone in isopropyl alcohol (250 ml) and benzene (200 ml) containing 10 mg of *p*-toluenesulfonic acid was heated while distilling off 200 ml of the isopropyl alcohol–benzene–water mixture. A solution of 50 ml of isopropyl alcohol in 50 ml of benzene was added and 100 ml of the isopropyl alcohol–benzene–water mixture was removed. The reaction mixture was then cooled and solid potassium carbonate added, filtered, and concentrated *in vacuo* giving a solid (30.8 g, 78%) characterized as 2-phenyl-6-isopropoxymethylenecyclohexanone, mp 74–75°. Due to the extreme lability of this compound

(28) Neither of these explanations of the exclusive production of the *trans*-propenyl product **12** and lack of trans diene in the reaction mixture at low and high conversion are totally satisfying. Thus, a more definitive answer to this question must await further studies. It is interesting that, in the acyclic analog of **5**, cis–trans isomerization predominates in the sensitized reaction and di-$\pi$-methane reaction pathways are inefficient.[3] On the contrary, sensitized photolysis of **5** leads to relatively efficient di-$\pi$-methane rearrangement. This difference between the triplet reactivity of acyclic and cyclic 1,4-dienes might be an important clue about the influence of structure on the fate of cyclopropyldicarbinyl diradicals.

(29) R. C. Hahn and L. J. Rotham, *J. Amer. Chem. Soc.*, **91**, 2409 (1969).

(30) W. S. Johnson, *et al.*, *ibid.*, **69**, 1361 (1947).

no further purification was attempted. The spectral data of this compound are the following: nmr ($CDCl_3$) $\tau$ 2.30 (s, 1 H, olefinic), 2.50–2.80 (m, 5 H, aromatic), 5.90 (h, $J$ = 6.5 Hz, 1 H, $CH(CH_3)_2$), 6.40 (t, 1 H, PhCH), 7.20–8.20 (m, 6 H, $CH_2$), 8.60 (d, $J$ = 6.5 Hz, 6 H, $CH_3$); ir ($CHCl_3$) 3.35, 3.37, 3.41, 3.50, 5.90, 6.05, 6.40, 6.70, 6.83, 6.90, 7.20, 7.30, 7.70, 8.15, 8.80, 9.10, 9.40, 10.25, 11.00, 11.30, 11.60, 12.00, 12.30, and 14.50 $\mu$.

**3-Phenylcyclohexene-1-carboxaldehyde (8).**[8] To a suspension of 4.1 g (0.11 mol) of lithium aluminum hydride in 350 ml of anhydrous ether was added, dropwise, an ether solution of 30.6 g (0.13 mol) of 2-phenyl-6-isopropoxymethylenecyclohexanone at 0° under nitrogen with stirring. The resulting mixture was stirred overnight at room temperature and after cooling to 0°, saturated sodium sulfate was added until a granular precipitate formed. The reaction mixture was then filtered into cold 10% sulfuric acid; the ether layer was separated and the water layer extracted with chloroform. The organic layers were combined, dried, and concentrated *in vacuo* giving 20.9 g (90%) of a slightly brown oil, characterized as 3-phenylcyclohexene-1-carboxyaldehyde. Attempts at further purification by distillation caused extensive polymerization of this material. The spectral data are the following: nmr ($CDCl_3$) $\tau$ 0.28 (s, 1 H, –COH), 2.45–2.70 (m, 5 H, aromatic), 3.10 (m, 1 H, CH=CC=O), 6.35 (m, 1 H, PhCH), 7.60–9.00 (m, 6 H, $CH_2$); ir ($CHCl_3$) 3.35, 3.44, 3.54, 5.95, 6.15, 6.30, 6.75, 6.95, 8.60, 8.80, 9.30, and 14.50 $\mu$.

The 2,4-dinitrophenylhydrazone derivative was prepared in the usual fashion and purified by recrystallization from 1:1 ethyl acetate–ethanol, mp 225–226.5°.

*Anal.* Calcd for $C_{19}H_{18}N_4O_4$: C, 62.29; H, 4.95; N, 15.29. Found: C, 62.47; H, 5.06; N, 15.26.

**1-Phenyl-3-methylcyclohexene-3-carboxaldehyde (9).** To a solution of 27.1 g (0.24 mol) of potassium *tert*-butoxide in 150 ml of *tert*-butyl alcohol was added 33.9 g (0.18 mol) of 3-phenylcyclohexene-1-carboxaldehyde and 52.09 g (0.37 mol) of methyl iodide in 65 ml of *tert*-butyl alcohol at 50°. The resulting mixture was stirred for 3 hr at 55° and then overnight at room temperature and water was added and the resulting solution extracted with ether. The ethereal extracts were washed with water, dried, and concentrated *in vacuo* giving 31.9 g of a slightly yellow oil which was subjected to chromatography on a 5 × 40 cm column, slurry packed with silica gel (Davison grade 923, 100–200 mesh) in hexane. Elution was with 2 l. of 5% ether–hexane, 1 l. of 10% ether–hexane, and 4 l. of 15% ether–hexane; 250-ml fractions were collected. Fractions 20–22 gave 8.82 g (23.2%) of a clear oil characterized as 1-phenyl-3-methylcyclohexene-3-carboxaldehyde. The spectral data of this compound are the following: nmr ($CDCl_3$) $\tau$ 0.47 (s, 1 H, COH), 2.40–2.60 (m, 5 H, aromatic), 4.20 (s, 1 H, olefinic), 7.40–7.70 (m, 2 H, allylic $CH_2$), 8.0–8.50 (m, 4 H, $CH_2$), 8.80 (s, 3 H, $CH_3$); ir (liq film) 3.25, 3.30, 3.41, 3.47, 5.80, 6.22, 6.68, 6.91, 11.00, 11.78, 13.21, and 14.35 $\mu$.

The 2,4-dinitrophenylhydrazone derivative was prepared in the usual fashion and purified by recrystallization from ether–hexane, mp 152–154°.

*Anal.* Calcd for $C_{20}H_{20}N_4O_4$: C, 63.15; H, 5.30; N, 14.73. Found: C, 63.31; H, 5.36; N, 14.75.

**1-Phenyl-3-methyl-3-(1-*cis*-propenyl)cyclohexene (5).** To a suspension of 24.8 g (0.07 mol) of triphenylethylphosphonium bromide in anhydrous ether was added 40 ml of a 1.67 $M$ solution of $n$-butyllithium under nitrogen. The resulting red solution was stirred for 1 hr and then an anhydrous ether solution of 8.82 g (0.04 mol) of 1-phenyl-3-methylcyclohexene-3-carboxaldehyde was added dropwise causing disappearance of the color and precipitation of the inorganic salts. The resulting solution was refluxed for 2 hr and stirred overnight; water was then added dropwise. The ethereal layer was separated, washed with water, dried, and concentrated *in vacuo* giving 9.78 g of an oil which was subjected to chromatography on a 2.5 × 58 cm column, packed with alumina (Alcoa F-20, 100–200 mesh) in hexane. Elution was with 2 l. of hexane; 250-ml fractions were collected. Fractions 2 and 3 gave 4.28 g (46%) of a clear oil characterized as 1-phenyl-3-methyl-3-(1-*cis*-propenyl)-cyclohexene. The spectral data are as follows: nmr ($CDCl_3$) $\tau$ 2.60–2.82 (m, 5, H, aromatic), 3.80 (m, 1 H, olefinic), 4.60–4.70 (m, 2 H, CH=CH), 7.50–7.80 (m, 2 H, allylic $CH_2$), 7.90–8.70 (m, 4 H, $CH_2$), 8.30 (d, $J$ = 5 Hz, 3 H, allylic $CH_3$), 8.80 (s, 3 H, $CH_3$); ir (liq film) 3.25, 3.35, 3.44, 6.28, 6.70, 6.93, 7.35, 9.35, 13.20, and 14.35 $\mu$; uv (acetonitrile) 248 nm ($\epsilon$ 17,900), 254 (17,000).

*Anal.* Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.32; H, 9.58.

**Photolyses of 1-Phenyl-3-methyl-3-(1-*cis*-propenyl)cyclohexene. Direct Irradiation.** A solution of 1.02 g (4.7 mmol) of 1-phenyl-3-methyl-3-(1-*cis*-propenyl)cyclohexene in 500 ml of hexane was purged with nitrogen for 30 min before and during the photolysis. The irradiation was carried out using a 450-W Hanovia medium-pressure lamp with a Corex glass filter, all in a water-cooled immersion well, for 9.5 hr. The solvent was removed *in vacuo* giving 1.05 g of a yellow oil which was then subjected to gas–liquid chromatography on a 12 ft × 0.25 in. (2% SE-30 on Chromosorb P, acid washed, 60–80 mesh) column maintained at 210°. Two major photoproducts were obtained along with recovered starting material (0.327 g, 31.1%) in the following quantities: major I (38 min retention time), 0.282 g (37.8%); and minor II (35 min retention time), 0.175 g (24.3%). The two photoproducts (I and II) displayed the following spectral data: major photoproduct (I) nmr ($CDCl_3$) $\tau$ 2.65 (s, 5 H, aromatic), 4.30–4.45 (m, 2 H, CH=CH), 7.80–8.46 (m. 7 H, $CH_2$'s and CH), 8.22 (d, 3 H, $J$ = 6 Hz, allylic $CH_3$), 9.00 (s, 3 H, $CH_3$); ir (liq film) 3.25, 3.27, 3.32, 3.37, 3.43, 3.50, 6.24, 6.72, 6.95, 7.30, 9.32, 13.20, and 14.30 $\mu$; uv (acetonitrile) 258 nm ($\epsilon$ 870); minor photoproduct (II) nmr ($CDCl_3$) $\tau$ 2.67 (s, 5 H, aromatic), 4.30–4.45 (m, 2 H, CH=CH) 7.80–8.46 (m, 7 H, $CH_2$'s and CH), 8.28 (d, 3 H, $J$ = 8 Hz, allylic $CH_3$), 9.20 (s, 3 H, $CH_3$); ir (liq film) 3.25, 3.27, 3.32, 3.37, 3.43, 3.50, 6.24, 6.72, 6.95, 7.30, 9.32, 9.75, 10.78, 13.20, and 14.30 $\mu$; uv (acetonitrile) 258 nm ($\epsilon$ 1120).

*Anal.* of I. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.34; H, 9.51.

*Anal.* of II. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.59; H, 9.46.

The structures of the above photoproducts (I and II) were determined to be the following: (I), 1-phenyl-5-methyl-6-*endo*-(2-*cis*-propenyl)bicyclo[3.1.0]hexane (**10**); (II), 1-phenyl-5-methyl-6-*endo*-(1-*trans*-propenyl)bicyclo[3.1.0]hexane (**12**), on the basis of their spectral properties and the degradation and independent synthetic sequences given below.

**Sensitized Irradiation.** A solution of 2.00 g (9.44 mmol) of 1-phenyl-3-methyl-(3-*cis*-propenyl)cyclohexene and 5.00 g (27.45 mmol) of benzophenone in 750 ml of acetonitrile was purged with nitrogen for 30 min before and during the photolysis. Irradiation was carried out using the same apparatus described above for 3.0 hr, however, with a Pyrex glass filter. After termination of the irradiation and solvent removal *in vacuo*, the 7.01 g of a slightly yellow oil was subjected to chromatography on a 2.5 × 50 cm column, slurry packed with silica gel (Davison, grade 923, 100–200 mesh) in 0.5% ether–pentane. Elution was with 2 l. of 0.5% ether–pentane; 250-ml fractions were collected. Fractions 5 and 6 gave 1.21 g of a clear oil which was then subjected to gas–liquid chromatography under the same conditions stated above. Only one photoproduct was obtained (0.78 g, 39.0%), characterized as 1-phenyl-5-methyl-6-*endo*-(1-*trans*-propenyl)bicyclo[3.1.0]hexane along with recovered starting material.[13]

**Structure Determination of Photoproducts I and II. Degradation of I to 1-Phenyl-5-methyl-6-*endo*-hydroxymethylbicyclo[3.1.0]hexane (14).** Ozone in an oxygen stream was passed through a pentane solution of 41.4 mg (0.2 mmol) of photoproduct I at −30° for 6 min. The crude ozonolysis solution was added dropwise to a solution of 7 mg (0.2 mmol) of lithium aluminum hydride in anhydrous ether at 0° under nitrogen. The reaction mixture was warmed to room temperature and stirred for 12 hr. After cooling to 0°, a saturated sodium sulfate solution was added until a granular precipitate formed, and the organic layer was separated, dried, and concentrated *in vacuo* giving 47.5 mg of a slightly brown oil which was subjected to preparative layer chromatography on silica gel (Brinkman, $PF_{254}$) using 20 × 20 cm plates. Two developments with 5% ether–pentane elution gave four overlapping bands which were cut and ether extracted. Concentration of each *in vacuo* gave the following: cut 1 ($R_f$ *ca.* 0.2), 20 mg (48%) of an oil characterized as 1-phenyl-5-methyl-6-*endo*-hydroxymethylbicyclo[3.1.0]hexane on the basis of its nmr and ir which were superimposable on those of synthesized material (see below) and by comparison of the glc retention time (104 min) with that of synthesized material (12; 2% SE-30 on Chromosorb P, acid washed, 60–80 mesh column maintained at 155°).

**Degradation of II to 1-Phenyl-5-methyl-6-*endo*-hydroxymethylbicyclo[3.1.0]hexane (14).** Ozone in an oxygen stream was passed through a pentane solution of 0.50 g (2.4 mmol) of photoproduct II at −30° for 1 hr. The crude ozonoylsis solution was reacted with lithium aluminum hydride and worked up and purified by the same method given above. Concentration *in vacuo* of the ethereal extracts of tlc cuts gave 0.06 g (12%) of an oil characterized as 1-phenyl-5-methyl-6-*endo*-hydroxymethylbicyclo[3.1.0]hexane on the basis of its nmr and ir which were superimposable on those of the synthesized material (see below) and by comparison of the glc retention time (104 min) with that of synthesized material on the same

column used above maintained at 155°. The material from other cuts was shown not to contain any of the exo isomer.

**1-Phenyl-2-methylcyclopentan-1-ol.** This compound was prepared by the method of Battioni and coworkers.[31]

**1-Phenyl-2-methylcyclopentene.** This compound was prepared by the method of Maggio and English.[32]

***endo*- and *exo*-1-Phenyl-5-methylbicyclo[3.1.0]hexane-6-carboxylic Acid (16 and 17).** To a solution of 10.25 g (0.07 mol) of 1-phenyl-2-methylcyclopentene in 10 ml of *n*-octane containing 2.56 g of copper powder at 125° under nitrogen was added dropwsie 15.1 g (0.13 mol) of ethyl diazoacetate. The reaction mixture was then heated at 125° for 1 hr. The copper powder was removed by filtration and the filtrate concentrated *in vacuo* giving a dark brown oil which was mixed with 100 ml of 10% sodium hydroxide and heated at 100° for 14 hr under nitrogen. The reaction mixture was cooled and extracted with ether, and the ethereal extracts were washed with 10% sodium hydroxide. The combined aqueous layers were acidified with concentrated hydrochloric acid and extracted with chloroform, and the chloroform extracts were dried and concentrated *in vacuo* giving 8.4 g of a brown oil which was subjected to chromatography on a 5 × 35 cm column, slurry packed with silica gel (Davison, grade 923, 100–200 mesh) in 10% ether–pentane. Elution was with 1 l. of 12% ether–pentane, 2 l. of 15% ether–pentane, 2 l. of 17% ether–pentane, 1 l. of 30% ether–pentane, and 1 l. of 50% ether–pentane; 250-ml fractions were collected. Fractions 12–13 gave 1.00 g of white solid, and 14–17 gave 1.28 g of a slightly yellow oil.

Fractions 12 and 13 after recrystallization from hexane yield 0.98 g (7%) of a white solid, mp 198–200°, characterized as 1-phenyl-5-methylbicyclo[3.1.0]hexane-6-*exo*-carboxylic acid (see below). The spectral data for this compound are as follows: nmr ($CDCl_3$) $\tau$ 2.79 (s, 5 H, aromatic), 7.80–8.28 (m, 7 H, $CH_2$'s and CH), 8.60 (s, 3 H, $CH_3$); ir ($CHCl_3$) 3.38, 3.42, 3.51, 5.95, 6.24, 6.70, 6.98, 8.10, 8.90, 9.10, and 14.30 $\mu$.

*Anal.* Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.92; H, 7.50.

Fractions 14–17 which contained mainly the endo acid were subjected to preparative layer chromatography on silica gel (Brinkman, $PF_{254}$) using 20 × 20 cm plates. Two developments with 15% ether–pentane elution gave three overlapping bands which were cut and ether extracted. Concentration *in vacuo* gave the following: cut 1 ($R_f$ *ca.* 0.2), 0.10 g; 2 ($R_f$ *ca.* 0.6), 0.56 g of an oil both containing mainly 1-phenyl-5-methylbicyclo[3.1.0]hexane-6-*endo*-carboxylic acid. Attempts at further prufiication of this acid failed. The total yield of *endo*-carboxylic acid was 0.66 g (4.6%). The spectral data for this isomer are as follows: nmr ($CDCl_3$) $\tau$ 2.80 (s, 5 H, aromatic), 7.40–8.35 (m, 7 H, $CH_2$'s and CH), 8.99 (s, 3 H, $CH_3$); ir (liq film) 3.30, 3.3, 3.48, 5.95, 6.24, 6.70, 6.98, 7.98, 8.20, 9.30, 9.70, 12.75, 13.20, and 14.30 $\mu$.

**1-Phenyl-5-methyl-6-*exo*-hydroxymethylbicyclo[3.1.0]hexane (15).** To a suspension of 0.60 g (16.0 mmol) of lithium aluminum hydride in 100 ml of anhydrous ether was added dropwise a solution of 0.50 g (2.3 mmol) of 1-phenyl-5-methylbicyclo[3.1.0]hexane-6-*exo*-carboxylic acid at 0° under nitrogen with stirring. The resulting mixture was stirred overnight at room temperature. Saturated sodium sulfate was added carefully followed by water and the ether layer was separated. The water layer was extracted with chloroform. The combined organic layers were concentrated *in vacuo* giving 0.48 g of a crystallizing oil which after recrystallization from pentane gave 0.40 g (86%) of 1-phenyl-5-methyl-6-*exo*-hydroxymethylbicyclo-[3.1.0]hexane, mp 65–66°. The spectral data for this compound are as follows: nmr ($CCl_4$) $\tau$ 2.90 (s, 5 H, aromatic), 6.42 (A of ABX, d of d, $J_{AX}$ = 7 Hz, $J_{AB}$ = 11 Hz, 1 H, CHOH), 6.80 (B of ABX, d of d, $J_{BX}$ = 11.0 Hz, 1 H, CHOH), 8.85 (s, 3 H, $CH_3$); ir ($CHCl_3$) 2.76, 2.90, 3.40, 3.50, 6.24, 6.70, 6.90, 7.20, 8.80, 9.32, 9.80, 10.10, and 14.35 $\mu$.

*Anal.* Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.24; H, 8.93.

**1-Phenyl-5-methyl-6-*endo*-hydroxymethylbicyclo[3.1.0]hexane (18).** 1-Phenyl-5-methylbicyclo[3.1.0]hexane-6-*endo*-carboxylic acid (0.60 g, 2.77 mmol) and 1.20 g (32 mmol) of lithium aluminum hydride were reacted by the same procedure used above. After work-up, 0.50 g of a slightly yellow oil was obtained and subjected to preparative layer chromatography on silica gel (Brinkman, $PF_{254}$) using 20 × 20 cm plates. Two developments with 5% ether–pentane elution gave five overlapping bands which were cut and ether extracted. Concentration *in vacuo* gave the following: cuts 3 and 4 ($R_f$ *ca.* 0.2–0.4), 0.31 g (55%) of an oil containing the 1-phenyl-5-methyl-6-*endo*-hydroxymethylbicyclo[3.1.0]hexane. The spectral data for this compound are as follows: nmr ($CCl_4$) $\tau$ 2.80 (s, 5 H, aromatic), 6.20 (d, $J$ = 7.5 Hz, 2 H, $CH_2OH$), 7.70–8.90 (m, 7 H, $CH_2$'s and COH), 9.05 (s, 3 H, $CH_3$); ir (liq film) 2.76, 2.90, 3.40, 3.50, 6.24, 6.70, 6.90, 7.20, 9.80, 10.10, and 14.35 $\mu$.

A portion of this material was further purified by glc (retention 104 min) on a 12 ft × 0.25 in. (2% SE-30 on Chromosorb P, acid washed, 60–80 mesh) column maintained at 155°.

*Anal.* Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.97; H, 9.01.

**Lanthanide Induced Shift Nmr Spectral Proof of Structure of *endo*- and *exo*-1-Phenyl-5-methyl-6-hydroxymethylbicyclo[3.1.0]-hexane.** The nmr spectra of both the endo and exo alcohols, obtained above, were taken in $CCl_4$ in the presence of an increasing molar ratio of europium trisheptafluorobutylpivaloylmethane ($Eu(fod)_3$) and the chemical shifts of the methyl and low-field methylene resonances recorded relative to TMS. A change in the molar ratio of $Eu(fod)_3$ to endo alcohol from 0.0 to 0.6 resulted in a $\Delta\nu$ for the methyl resonance of 139 Hz and a $\Delta\nu$ for the low-field methylene resonance of 247 Hz. This is compared to the exo alcohol which displayed a $\Delta\nu$ for the methyl resonance of 241 Hz and a $\Delta\nu$ for the low-field methylene resonance of 109 Hz on changing from 0.0 to 0.75 molar ratio of $Eu(fod)_3$. These results are summarized above in Figure 1.

**Quenched Photolyses of 1-Phenyl-3-methyl-3-(1-*cis*-propenyl)-cyclohex-1-ene with 2,5-Dimethyl-2,4-hexadiene.** Solutions of 150 mg of 1-phenyl-3-methyl-3-(1-*cis*-propenyl)cyclohex-1-ene ($1.57 \times 10^{-2}$ *M*) and varying concentrations of 2,5-dimethyl-2,4-hexadiene in 45 ml of a cyclohexane solution in degassed sealed quartz tubes on a merry-go-round type apparatus were irradiated using a 450-W Hanovia immersion lamp with Corex glass filter centered between the revolving tubes. Irradiations were conducted from between 12 and 18 hr which led to starting material conversion of *ca.* 10–15%. After these periods the photolysates were concentrated *in vacuo* and the resulting mixtures diluted to 10.0 ml. The components were then quantitatively analyzed by glc giving the results summarized in Table I and Figure 2.

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## Appendix

**Derivation of Modified Stern–Volmer Relationship for the Cis–Trans Ratio of 1-Phenyl-5-methyl-6-*endo*-(1-propenyl)bicyclo[3.1.0]hexane.** From the following sequence based upon the assumption that the *trans*-propenyl product (**12**) results from the triplet excited state of the propenylcyclohexene (**5**) and the normal

$$5^0 \xrightarrow{I} 5^1 \qquad I$$

$$5^1 \xrightarrow{k_1} \mathbf{10} \qquad k_1[5^1]$$

$$5^1 \xrightarrow{k_{ds}} 5^0 \qquad k_{ds}[5^1]$$

$$5^1 \xrightarrow{k_{ISC}} 5^3 \qquad k_{ISC}[5^1]$$

$$5^3 \xrightarrow{k_{dt}} 5^0 \qquad k_{dt}[5^3]$$

$$5^3 \xrightarrow{k_3} \mathbf{12} \qquad k_3[5^3]$$

$$5^3 + Q \xrightarrow{k_q} 5^0 + Q^3 \qquad k_q[5^3][Q]$$

steady-state assumptions, the quantum yields for photoproducts **12** and **10** production are:

$$\Phi_{12} = \frac{k_3 k_{ISC}}{(k_{dt} + k_3)(k_{ds} + k_1 + k_{ISC})}$$

$$\Phi_{10} = \frac{k_1}{k_{ds} + k_1 + k_{ISC}}$$

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Thus, the unquenched product ratio is

$$R_u = \frac{\Phi_{10}}{\Phi_{12}} = \frac{10}{12} = \frac{k_1(k_{dt} + k_3)}{k_3 k_{ISC}}$$

Since the quantum yield for production of **12** in the presence of quencher is

$$\Phi_{12} = \frac{k_3 k_{ISC}}{(k_{dt} + k_3 + k_q[Q])(k_{ds} + k_1 + k_{ISC})}$$

the quenched product ratio becomes

$$R_q = \frac{\Phi_{10}}{\Phi_{12}} = \frac{10}{12} = \frac{k_1(k_{dt} + k_3 + k_q[Q])}{k_3 k_{ISC}}$$

Thus, the ratio of the quenched and unquenched quantum yield or the product ratios will depend upon the quencher concentration according to eq 1.

If the original assumptions are correct, *i.e.*, that photoproduct **10** results from the singlet and **12** from the triplet of **5**, a plot of $R_q/R_u$ *vs.* quencher concentration should be that of a straight line.

# The Kinetics, Stereochemistry, and Mechanisms of the Silaallylic and Silapropynylic Rearrangements

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**Abstract:** The unimolecular, gas-phase reaction kinetics of the silaallylic rearrangement, the complete absence of β-substituent rate effects, the lack of influence on the activation parameters in substituting phenyl for methyl at the silicon reaction center, and the failure to realize a bimolecular isomerization mode all point to a concerted, symmetrical transition state of silicon migration. The only substituent rate effects observed are readily correlated with steric strain relief (in the α position of the allyl side chain) and conjugation influences which reflect in the transition state the energy differences between products and reactants. These results stand in sharp contrast to those noted in the thiaallylic rearrangement where d orbital involvement in the formation of a dipolar reaction intermediate has been implicated. Stereochemical studies using optically active as well as deuterium labeling of the course of rearrangement show that every act of migration is accompanied by inversion of the silicon configuration. This indicates a preference for utilizing a 3p orbital in bridging the allylic structure with conservation of orbital symmetry. It is the first case of 1,3 or 1,5 migration of silicon in which the preference for 3p orbital utilization has been identified. The corresponding silapropynylic rearrangement involving silicon migration across the termini for a propargyl–allenyl grouping has also been realized (for the first time) in these investigations. The kinetic characteristics of this reaction indicate a symmetrical, concerted transition state, similar in all respects to the silaallylic rearrangement despite the need for bending of the propargyl–allenyl framework in the activation step. Moreover, stereochemical studies confirm that the process of migration again takes place with complete inversion of the silicon configuration, apparently uncontaminated by any competing pathways which might lead to retention and racemization. A carboallylic migration in simple olefinic analogs of silaallylic substrates does not take place with sufficient mobility to compete with homolytic fragmentation reactions. The vastly greater activation barrier of the carboallylic *vs.* the silaallylic perhaps may be correlated with the dissociation energy of the critical bond of the sigmatropic process.

The identification of a 1,3 sigmatropic migration of silicon in allylsilanes has been reported[1] in a preliminary communication. Therein, also, the importance of determining the stereochemistry of the rearrangement course was pointed out. Orbital symmetry[2] considerations require that thermal, suprafacial 1,3 rearrangements[3] of carbon undergo inversion of configuration at the migrating center in a process involving both lobes of an antisymmetric 2p orbital. On the other hand, 1,5 migrations[4] proceed with retention of configuration in utilizing only one lobe of the 2p orbital.

For migrations of silicon, the group IVb neighbor of carbon, the situation is more complex because of the availability of low-lying, empty 3d orbitals, and schemes which predict either retention or inversion can be readily conceived. The involvement of the analogous 3d orbitals in sulfur has been established[5] in the case of

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