nitrogen was added a 0.57 *M* tetrahydrofuran solution of sodium anthracene until the blue color persisted. This solution was allowed to stir for 2 hr and was subsequently quenched by exposure to the atmosphere. Pentane (100 ml) was added and the resulting mixture was filtered. The filtrate was washed with water (4 × 250 ml), dried, and evaporated under a packed column. The residue was chromatographed on an alumina column (pentane elution) and the eluate was again carefully concentrated. This residue was purified by preparative scale vpc (0.25 in. × 6 ft 5% SF-96, 120°) to give 670 mg (37%) of [4.4.2]propell-3-ene: ν_{max}^{neat} 2900 and 1450 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.68–5.80 (m, 2, olefinic) and 1.2–2.1 (m, 16).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.68; H, 11.26.

The *cis*-11,12-dideuterio derivative **46** was prepared analogously using sodium borodeuteride and propionic acid-d_1.

The conversion of **46** to **47** was achieved by the same procedure as that utilized in the transformation of **42** to **43** with identical results.

Acknowledgment. The partial support of the National Cancer Institute (Grant CA 12115) is acknowledged with gratitude.

Stereochemical Features of the Thermal and Photochemical Fragmentations of [4.4.2]Propella-2,4-dienes

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Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received February 23, 1972*

Abstract: Vapor-phase pyrolysis of several 11,12-disubstituted [4.4.2]propella-2,4-dienes has been found to result in clean fragmentation to tetralin and an olefinic component. Photofragmentation under singlet conditions also leads to substantial tetralin formation, although some ($_\sigma 2 + {}_\sigma 2$) cleavage in the opposite direction is now encountered. The isomer distributions of the methyl 2-deuteriovinyl ether and 1,2-dideuterioethylene so produced have been measured and significant stereoselectivity is observed. The level of stereocontrol is seen, however, to vary with the method of inducing fragmentation and with the geometry of the starting propelladiene. These observations are discussed in terms of the behavior of 1,4-diradical intermediates.

By 1961, preliminary insight into the mechanism of the thermal fragmentation of cyclobutanes to ethylenes began to emerge as the direct result of the pioneering studies of Walters.[2] In particular, Gerberich and Walters noted that although *cis*-1,2-dimethylcyclobutane did experience partial isomerization to its trans counterpart in the temperature region 380–430°,[3] the isolated 2-butene (64% cis and 36% trans) differed significantly in stereochemical composition from that of the equilibrium mixture (43–47% cis at these temperatures). Additionally, pyrolysis of *trans*-1,2-dimethylcyclobutane was seen to afford 2-butene composed chiefly, but not exclusively, of the trans isomer (89%).[4] The reasonable argument was advanced "that if a biradical exists momentarily as an intermediate, it decomposes before the original geometry is completely converted to the equilibrium distribution."

Nearly a decade later, Woodward and Hoffmann called attention to the theoretical possibility that the fragmentations of four-membered rings could proceed concertedly by the simultaneous stretching of two opposite bonds to furnish olefinic products directly.[5] This particular application of orbital symmetry theory revealed convincingly, however, that simple [$_\sigma 2_s + {}_\sigma 2_s$] fragmentation was unallowed for the concerted thermal reaction. Rather, synchronous rupture was demonstrated to require appreciable prior twisting of the cyclobutane ring in a manner which effectively inverts the stereochemistry of one of the constituent carbons at the transition state. At the time, *bona fide* experimental tests of this intriguing stereochemical implication were not available because of a lack of cyclobutane derivatives bearing sufficient stereochemical labeling.

The recent studies of Baldwin,[6] Frey,[7] and Paquette[8] with fused ring systems have given evidence that 1,4-diradical intermediates are likely involved, except when the proper juxtapositioning of an additional weak σ bond effectively obviates the need for the [$_\sigma 2_a + {}_\sigma 2_s$] mechanism. By and large, the structural features present in the cyclobutane derivatives pyrolyzed to date[9] have been such, however, that bond rotation, ring closure, and bond scission processes are reasonably competitive.[10]

Unfortunately, the inherently transient nature of 1,4 diradicals renders their detection and study by standard methods exceedingly difficult. Consequently, their intervention is frequently surmised on the basis of thermodynamic,[11] kinetic, and stereochemical grounds.

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(1) Phillips Petroleum Fellow, 1970–1971; University Dissertation Fellow, 1971–1972.

(2) The historic work of the Walters group on cyclobutane fragmentations date back to 1951: C. T. Genaux and W. D. Walters, *J. Amer. Chem. Soc.*, 73, 4497 (1951).

(3) H. R. Gerberich and W. D. Walters, *ibid.*, **83**, 3935 (1961).

(4) H. R. Gerberich and W. D. Walters, *ibid.*, **83**, 4884 (1961).

(5) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 65 ff.

(6) J. E. Baldwin and P. W. Ford, *J. Amer. Chem. Soc.*, **91**, 7192 (1969).

(7) A. T. Cocks, H. M. Frey, and I. D. R. Stevens, *Chem. Commun.*, 458 (1969).

(8) L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, **93**, 4922 (1971).

(9) For reviews, consult: (a) H. M. Frey, *Advan. Phys. Org. Chem.*, 4, 147 (1966); (b) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).

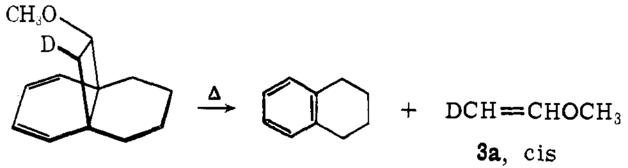
(10) (a) L. M. Stephenson and J. I. Brauman, *J. Amer. Chem. Soc.*, **93**, 1988 (1971); (b) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).

(11) (a) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961); **46**, 4920 (1967); (b) S. W. Benson and P. S. Nangia, *ibid.*, **38**, 18 (1963); (c) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, 1, 221 (1969).

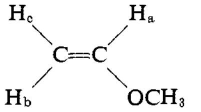
In this connection, the recent extended Hückel studies of such reactive intermediates by Hoffmann and coworkers[12] have led to the somewhat unanticipated conclusion that they are not true minima on the energy surface. Rather, the calculations of the Cornell group have suggested that tetramethylene diradicals are unstable with respect to olefin pairs and lack the possibility for interception or diversion. Such entities have been termed twixtyls.

In an effort to derive stereochemical evidence on the behavior of 1,4 diradicals, the thermal and photochemical fragmentations of several [4.4.2]propella-2,4-dienes have been examined.[13] As noted in the preceding paper,[14] the cyclobutane rings in these tricyclic molecules are sufficiently constrained in the conformational sense that concerted [$_\sigma 2_s + {_\sigma 2_a}$] retrogressions become highly unlikely. Consequently, the intervention of tetramethylene diradicals was anticipated. Also, in view of the fact that initial bond homolysis in these systems leads to semistabilized cyclohexadienyl radicals, some reduction in activation energy could accrue and be reflected in the need for lower pyrolysis temperatures.[15]

Pyrolysis Studies. Vapor-phase pyrolysis of **1** by slow introduction into a heated quartz tube (28 cm × 16 mm) packed with quartz chips (contact time ~2 min) at 760 Torr proceeded in high yield to afford tetralin (**2**) and methyl 2-deuteriovinyl ether (**3**). The aromatic hydrocarbon was identified by preparative vpc isolation and spectral comparison with an authentic sample. Ether **3** was transferred on a high vacuum line to an nmr tube containing $CDCl_3$–TMS. The cis–trans isomer distributions in the various samples were then established by quantitative integration of expanded scale nmr spectra taken at 100 MHz. Methyl vinyl ether displays three well-separated absorptions (ABX pattern) for its olefinic protons,[16] a precondition well suited to the accurate determination of the site of deuterium substitution.[17] In the present study, the extent of isotopic labeling at H_b and H_c in **3** was assessed quantitatively only after making careful allowance for the small amounts of nonlabeled methyl vinyl ether present in the various samples (see Experimental Section). The results are summarized in Table I. The reaction has been studied at two temperatures and at least two runs were carried out at each temperature. Appropriate control experiments with unlabeled propelladienes served to conform the absence of observable syn–anti isomerization of the methoxyl group under the thermal activation conditions. Also, the geometric isomers of **3** were shown not to experience interconversion at these temperatures and residence times.



1 **2** **3a**, cis; **b**, trans



$$\begin{array}{ccc} H_c & & H_a \\ & C{=}C & \\ H_b & & OCH_3 \end{array}$$

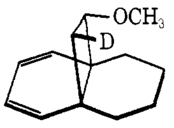
J_{ab} = 14.4 Hz; J_{ac} = 6.6 Hz; J_{bc} = −2.2 Hz

Table I. Thermally Generated Isomer Distributions of **3**

Reactant	Temp, °C	Relative % yield **3a**	Relative % yield **3b**
1	245	98	2
	314	97	3
4	245	80	20
	314	77	23
1 + **5**[a]	314	29	71

[a] The **1**:**5** ratio was 26:74.

The thermal fragmentation of **4** also gave rise cleanly to tetralin and **3**. Interestingly, propelladiene **4** exhibited only a 79% preference for the [$_\sigma 2_s + {_\sigma 2_s}$] pathway (Table I). This contrasts with the exceptionally high levels of double retention exhibited by **1** and **5**. It is to be recalled that the synthetic method employed in the preparation of **5** provided material of 74% geometric purity, with the minor isomer being **1** (26%).[14] Nevertheless, because of the high level of stereoselectivity observed in the fragmentation of **1**, proper normalizations can be applied to the data derived from the pyrolysis of this mixture in order to delineate the stereochemical course of the cycloreversion exhibited by **5**.



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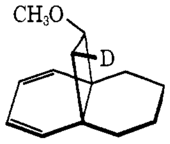

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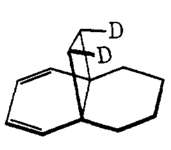
Under conditions where the 11,12-*cis*-dideuteriopropelladienes **6** and **7** (as a 3:2 mixture[14]) were similarly introduced slowly into the pyrolysis tube (310°), cleavage to tetralin and the 1,2-dideuterioethylenes was again uncomplicated by side reactions. For analysis, the labeled ethylenes were transferred on a high-vacuum line to nmr tubes containing CCl_4–10% TMS (0.3 ml/tube). The relative proportions of the geometric iso-



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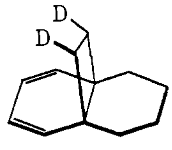

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[12] R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970).

[13] The results of our pyrolysis studies have appeared in preliminary form: L. A. Paquette and G. L. Thompson, *ibid.*, **93**, 4920 (1971).

[14] L. A. Paquette and G. L. Thompson, *ibid.*, **94**, 7118 (1972).

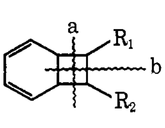
[15] The possible magnitude of this effect is somewhat difficult to estimate. It is recognized that there is an activation barrier for addition of free radicals to benzene and other aromatic rings (M. Szwarc and J. H. Binks, "Theoretical Organic Chemistry," Kekule Symposium, 1958, Butterworths, London, 1958, pp 263 ff). From microscopic reversibility considerations, there must therefore exist a small but significant barrier for loss of a group from substituted cyclohexadienyl radicals.

[16] R. T. Hobgood, Jr., G. S. Reddy, and J. H. Goldstein, *J. Phys. Chem.*, **67**, 110 (1963); C. N. Banwell, N. Sheppard, and J. J. Turner, *Spectrochim. Acta*, **16**, 794 (1960); W. Brugel, Th. Ankel, and F. Kruckeberg, *Z. Electrochem.*, **64**, 1121 (1960).

[17] For a detailed analysis of the nmr spectra of several mono- and dideuterated derivatives of methyl vinyl ether, see J. R. Dombroski and C. Schuerch, *Macromolecules*, **3**, 257 (1970).

mers were subsequently determined by deuterium-decoupled proton nmr spectroscopy.[18] The relative intensities of the singlet absorptions due to *cis*- (532.1 Hz)[19] and *trans*-1,2-dideuterioethylene (532.7 Hz)[19] indicated that 66 ± 1% of the cis isomer was present in the pyrolysis mixtures. Earlier investigation has established that cis–trans interconversion of 1,2-dideuterioethylene is inoperative up to 450° under similar conditions.[6,20] Consequently, **6** and **7** exhibit a strikingly lower selectivity than the related methoxy derivatives **1**, **4**, and **5**.

Photochemical Investigations. Photoinduced fragmentations of the bicyclo[4.2.0]octa-2,4-diene ring system **8** have commanded only passing attention,[21-26] despite the fact that the intrinsic stereochemical features of such reactions are of considerable theoretical interest. Perhaps this is because two modes of bond cleavage have been observed and the factors controlling the predominant pathway in a given example are not yet fully understood. For example, whereas direct irradiation of the *trans*-7,8-diacetoxy (**8a**)[21] and *cis*,-*endo*-7,8-dimethyl (**8b**)[22] derivatives of **8** leads exclusively to 1,8-disubstituted octatetraenes *via* path b, appropriate triplet sensitization of **8a** results uniquely in operation of the type a process.[23] However, this fragmentation mode is also encountered from the singlet excited states of **9** and **10** which give rise to benzonitrile (>90%)[24] and naphthalene (~100%),[25] respectively.



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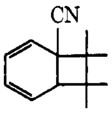

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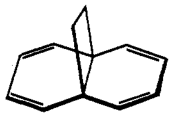

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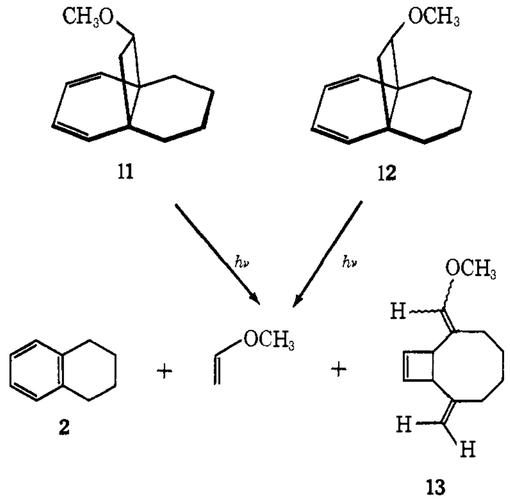
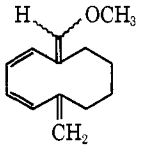
We have observed that Corex-filtered irradiation (200-W Hanovia medium-pressure Hg arc, 8.0 hr) of degassed 0.02 *M* diglyme solutions of **11** and **12**[14] in sealed quartz tubes at ambient temperature affords chiefly tetralin (**2**) and methyl vinyl ether, together with lesser amounts (*ca.* 18%) of a somewhat unstable substance which has tentatively been assigned structure **13**. Accurate mass measurement (calcd *m/e* 190.1357, found *m/e* 190.1357) indicated it to be isomeric with **11** and **12**. The ultraviolet spectrum showed only intense end absorption without maxima (ε 310 at 260 nm). In the nmr spectrum, there was displayed a sharp two-proton singlet at δ 6.20 typical of olefinic cyclobutene hydrogens[27] and a broadened singlet of area 2 at 4.62 expected of a terminal methylene group. The =CH-(OCH$_3$) proton appeared at δ 5.68 and consisted again of a somewhat broadened singlet. The remaining portion of the spectrum was comprised of a methoxyl singlet at δ 3.50, a broad singlet of area 2 at δ 2.99 due to the doubly allylic protons, and a multiplet in the δ 1.1–2.4 region attributable to the eight methylene hydrogens. It is plausible that **13** arises from initial cleavage of **11** and **12** along the two central bonds to afford **14** which subsequently experiences photoinduced disrotatory cyclization.





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To gain information on the stereochemistry of the type a fragmentation in **11** and **12**, similar photolyses of the suitably labeled propelladienes **1**, **4**, and **5** have been carried out (Table II). Upon completion of each irradiation, the contents of the tube were transferred under vacuum at 25° and the higher boiling components were collected at −60°. The more volatile material which condensed at −196° was subsequently transferred (10^{-4} Torr) to a semimicro nmr tube containing CCl$_4$–TMS (0.03 ml) and analyzed by the nmr method described above. Substantial care was taken to preclude the incidence of radiation at wavelengths below 280 nm in order that only the diene [for **11**, $\lambda_{\max}^{\text{isooctane}}$ 269 nm (ε 3050); for **12**, $\lambda_{\max}^{\text{isooctane}}$ 274 nm (ε 2500)] experience photoexcitation and that the derived tetralin not be capable of playing the role of sensitizer. Control experiments attested to the stability of the

Table II. Photochemically Generated Isomer Distributions of **3**

Reactant	Relative % yield **3a**	**3b**
1	88	12
4	98	2
1 + **5**[a]	31	69

[a] The **1**:**5** ratio was 26:74.

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[18] We were initially made aware of this elegant method of analysis through the courtesy of Professor Gerhard Closs, whom we also thank for the actual spectral determinations cited herein.

[19] Downfield from TMS at 100 MHz.

[20] Equilibration of *cis*- and *trans*-1,2-dideuterioethylene from both directions through the agency of $^3SO_2$ at 26° has recently been shown to favor the cis isomer slightly (0.511 ± 0.011): C. Badcock and J. Calvert, private communication on Dec 2, 1971.

[21] D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959).

[22] K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **93**, 2073 (1971).

[23] R. A. Caldwell, *J. Org. Chem.*, **34**, 1886 (1969).

[24] J. G. Atkinson, D. E. Ayer, G. Büchi, and E. W. Robb, *J. Amer. Chem. Soc.*, **85**, 3257 (1963).

[25] J. Altman, E. Babad, D. Ginsburg, and M. B. Rubin, *Isr. J. Chem.*, **7**, 435 (1969).

[26] G. Schröder, *Chem. Ber.*, **97**, 3140 (1964).

[27] Consult, for example, L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **93**, 5735 (1971).

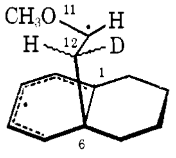
methoxypropelladienes and labeled vinyl ethers under these reaction conditions.[28]

As the data of Table II show, **4** exhibits a marked preference for stereospecific photofragmentation, whereas isomers **1** and **5** in which the methoxyl group is positioned above the cyclohexadiene ring do not. The product distributions then emerge as significantly different in a stereochemical sense from those realized in the purely thermal fragmentations.

Discussion

The data of Tables I and II reveal that the thermal and photochemical fragmentations of the 11-methoxy-[4.4.2]propella-2,4-dienes are both stereoselective. A subtle but meaningful difference is encountered, however, in the behavior of **1** and **4**. Whereas syn isomer **1** gives evidence of diminishing stereoselectivity in proceeding from the pyrolytic to the photolytic reaction, the decomposition of anti isomer **4** develops increased stereoselectivity. The most economical explanation of these and the other observations described above appears to reside in the reactivity characteristics of the stereochemically distinguishable semistabilized 1,4 diradicals which seemingly intervene in these bond scission processes.

Initial cleavage in the 11-methoxypropelladienes is anticipated at C_1–C_{11} since the activation energies of homolytic reactions are related fundamentally to the resonance energies which develop in the resulting diradicals.[10b,29] In the case of that diradical **15** derivable from **1** and **5**, subsequent irreversible cleavage of the C_6–C_{12} bond to product tetralin under the conditions of thermal activation is evidently much faster than C_{11}–C_{12} bond rotation. Two important factors perhaps contribute to the high $k_{\text{scis}}/k_{\text{rot}}$ encountered in these examples. Firstly, C_{11}–C_{12} bond rotation would require the methoxy group to migrate from a site over the diene unit where it is sterically unencumbered to a position over the tetramethylene bridge where serious compression with the axially disposed methylene hydrogens will be engendered. The untoward effect of such nonbonded repulsive interactions is certain to constitute an appreciable barrier to internal rotation. Secondly, the methoxyl group is a rather massive rotor and a bias in favor of k_{scis} should be accentuated by the sheer ponderal effect associated with this type of substitution.[30]



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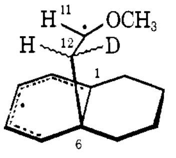

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The not insignificant role of such steric factors would appear to be supported by the behavior of **4**. Initial rupture of the C_1–C_{11} bond in this example leads initially to **16** in which the methoxyl substituent is constrained into space occupied by at least one axial hydrogen.[14] Bond rotation in the 1,4 diradical to arrive at thermodynamically more favorable conformation **15** now becomes reasonably competitive with k_{scis}. The importance of ponderal effects as they relate to increased rotational barriers in these systems is revealed convincingly by the thermal behavior of **6** and **7**. Although the predominant course of their cycloreversions occurs in a stereochemical sense compatible with $k_{\text{scis}} > k_{\text{rot}}$, such $[{}_{\sigma}2_s + {}_{\sigma}2_s]$ elimination of ethylene is only marginally favored. Rather, it would appear that bond rotation and cleavage now compete quite favorably.

In the photochemical processes, the partial loss of stereoselectivity attending the fragmentation of **1**, particularly as it contrasts with the high stereoselectivity encountered with **4**, points to an *apparent* crossover in the relative bulks of the cyclohexadienyl and cyclohexyl rings in the excited state. This unprecedented behavior could perhaps find its origin in the nonisoenergetic ground-state conformations of **1**, **4**, and **5** or in one or more of the electronic and structural perturbations possibly associated with the singlet π–π^* excited states of these unsaturated propellanes. Along these latter lines, one imaginable interpretation is that the S_1 state of **4** experiences efficient and potentially concerted $[{}_{\sigma}2_s + {}_{\sigma}2_s]$ cyclobutane fragmentation in the manner anticipated from orbital symmetry considerations.[5] In the syn series (**1** and **5**), charge-transfer interaction of the proximate methoxyl group with the S_1 excited state of the cyclohexadiene ring could allow for the incursion of a modest amount of intersystem crossing and subsequent stepwise fragmentation from the T_1 state. While we recognize that intersystem crossing of $S_1 \rightarrow T_1$ is not generally observed in olefinic systems, the special geometry inherent in **1** and **5** could conceivably lend itself to partial ($\leq$20–25%) operation of this competitive pathway. However attractive, such an electronic effect of the *syn*-methoxyl group appears to be of marginal importance, since the ultraviolet spectra of the two isomers are quite comparable (*vide supra*).[31]

Alternatively, should the first excited state (ψ_3) of the propelladienes exhibit the usual propensity of conjugated dienes for 1,3 bonding,[32] the conformational features of the customarily planar 1,3-cyclohexadiene chromophore could be transmuted into a nonplanar, twisted ring system with substantially enhanced space-filling character. As a result, the intrinsically less congested topology of the cyclohexane ring which develops upon photoexcitation would be such as to encourage movement of the methoxyl substituent into that particular region of space. Loss of stereochemical integrity in such quasi-concerted[33] reactions would then be expected to occur uniquely from the syn isomers as observed. Although it is difficult to unambiguously rule out contributions from this particular phenomenon at this time, the present results seem most comprehensible in terms of the hypothesis suggested by Stephenson and Brauman.[10a]

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(28) Leakage (4%) of *cis*- to *trans*-HDC=CHOCH₃ was noted after extending the photolysis for a period exceeding by a factor of 3 the normal reaction time (8 hr). This behavior could account for the 2% loss in stereochemistry observed in the case of **4**.

(29) D. A. Bittker and W. D. Walters, *J. Amer. Chem. Soc.*, 77, 1429 (1955).

(30) A previous application of ponderal and energetic effects to 1,4 diradicals has been advanced by J. A. Berson, D. C. Tompkins, and G. Jones, III, *ibid.*, 92, 5799 (1970).

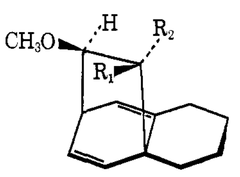
(31) Compare also the electronic spectrum of [4.4.2]propella-2,4-diene: $\lambda_{\text{max}}^{\text{isooctane}}$ 272 nm (ϵ 3000).

(32) R. Srinivasan and S. Boué, *J. Amer. Chem. Soc.*, 93, 5606 (1971), and references cited therein.

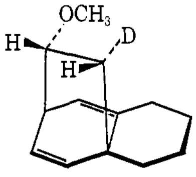
(33) J. P. Freeman, D. G. Pucci, and G. Binsch, *ibid.*, in press.

Thus, for reasons discussed above, thermally generated **15** faces a relatively high barrier to rotation and a relatively low barrier to fragmentation. It is likely that the frequency factors for these processes likewise favor bond cleavage. As the amount of internal energy in this diradical is increased (*e.g.*, upon photoexcitation), the highly stereocontrolled reaction can be expected to become less selective as the existing differences in activation energy become partially damped out. In **16**, the pyrolysis results reveal that the barriers to rotation and fragmentation are more comparable, although the frequency factors probably still favor cleavage. The higher energy process (photolysis) in this case will, however, again damp out the control of potential energy,[34] making the reaction more stereoselective as the energy content of the molecule increases, in line with our observations.

Mention should also be made of the fact that the available thermochemical data do not rule out the possible operation of preliminary [1,3] sigmatropic rearrangement to give intermediates of type **17** which subsequently undergo stereospecific Diels–Alder fragmentation. To conform with experimental fact, however, it is necessary to assume that **1** and **5**, which are predisposed with *syn*-methoxyl groups, undergo this prerearrangement with high levels of configurational retention to provide **17a** and **17b**, respectively. In contrast, **4** which possesses an *anti*-11-methoxyl group would have to experience some inversion of configuration to furnish the appropriate mixture of **17b** and **17c**. Although a previous example of such alteration in the retention–inversion characteristics of a thermal [1,3] sigmatropic shift has been reported,[35] the high propensity of structurally related dienes[36] for symmetry-allowed thermal [1,5] sigmatropic rearrangement leads us to conclude that this interesting alternative is not likely to gain importance.



17a, $R_1 = D$; $R_2 = H$
b, $R_1 = H$; $R_2 = D$



17c

Thus, it has been demonstrated with 1,4 diradicals in which k_{scis} has been enhanced appreciably relative to k_{rot} that partial loss of stereochemical integrity does result during fragmentation. Moreover, the varying levels of stereoselectivity encountered in the thermal and photochemical fragmentations reveal that the ultimate fate of such tetramethylene diradicals can be measurably controlled by judicious choice of their method of generation. Accordingly, the present results are qualitatively concordant with two descriptions of these singlet diradicals: (a) such species are not accurately represented by twixtyls,[12] *i.e.*, as reasonably flat regions atop a potential surface; rather, these areas of potential energy space are more precisely characterized by maxima and minima which reflect such subtle intrinsic molecular features as steric demands and ponderal effects; or (b) such intermediates are in fact, as suggested by Hoffmann,[12] large energetically flat regions which, however, are extremely sensitive to the trajectory taken by the incipient diradicals as they enter onto this plateau. In this event, the absence of minima and maxima may well cause the "momentum" distribution at the point of entry into the flat region to control the ultimate distribution of geometrically isomeric olefins.[37] Further work is obviously needed before these ambiguities are resolved.

Experimental Section

General Pyrolysis Procedure. A 50-mg sample of the propelladiene was gradually introduced into a quartz tube (28 cm × 16 mm) packed with quartz chips maintained at the desired temperature under a small flow of nitrogen (~0.10–0.15 ml/sec) at 760 Torr. Tetralin was collected in an air-cooled trap, and ethylene or methyl vinyl ether was trapped in a more remotely positioned portion of the "transfer unit"[38] cooled in liquid nitrogen. Upon completion of the pyrolysis (10–15 min), the fore-end of the Pyrex "transfer unit" was sealed, the unit was attached to a high vacuum line, the collection tube and the nmr tube receiver (containing *ca.* 0.3 ml of solvent and TMS as internal standard) were cooled to −196°, and the system was evacuated at 10^{-4} mm for 40 min. The transfer unit was isolated from the vacuum line, the collection section of the unit was allowed to warm to room temperature, and after completion of the transfer the cold nmr tube was carefully sealed.

Analysis of the isomer distribution in **3** was achieved by careful integration of 100-MHz nmr spectra in the δ 3.7–4.2 region at 50-Hz sweep width. The spectrum of unlabeled **3** appears as two doublets of doublets in this region. The spectrum of a cis,trans mixture of **3** containing 100% d_1 would appear as two doublets, the ratio of which would provide the cis–trans ratio directly. Since the present samples were contaminated with d_0 material, the actual spectra showed the additional doublet of doublets. The upfield resonance of each doublet due to d_0 contaminant was superimposed upon the corresponding resonance of the d_1 product. Accordingly, the true areas of the peaks due to the d_1 species were derived by subtracting from each one the area of its downfield "echo" resonance.

General Photolysis Procedure. The photolyses were performed in sealed quartz tubes suitable for use on a high vacuum line. The light source was a 200-W medium-pressure Hanovia lamp, the emission from which was passed through a Corex filter. The propelladienes were irradiated for 8.0 hr as 0.02 *M* degassed solutions in purified diglyme (a high boiling solvent was used to facilitate isolation of the volatile components) at ambient temperature. Upon completion of the reaction, the contents of the photolysis vessel were distilled under vacuum at 25°; the higher boiling components were collected at −60° and the volatiles were trapped at −196°. The latter were transferred (10^{-4} Torr) to a semimicro nmr tube containing CCl_4–TMS (0.03 ml) and analyzed as above. Samples prepared in this manner were entirely free of solvent and recovery was nearly quantitative. The less volatile material including a small amount remaining in the photolysis vessel was diluted with pentane, washed well with water, and analyzed by vpc.

Preparative scale isolation of **13** (5 ft × 0.25 in. Al column packed with 5% SE-30 on Chromosorb G at 105°) gave material with the spectra outlined in the text. When **1**, **4**, and **5** were photolyzed and

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(34) That is to say that the influence of the ΔE_a term which is highly important to the outcome of the thermal reactions (stereochemically speaking in the present context) is less so when the same species is excessively vibrationally excited.

(35) (a) J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **92**, 1096 (1970). (b) We thank Professor Berson for an enlightening exchange of information on this point.

(36) (a) J. A. Berson and M. R. Wilcott, III, *J. Amer. Chem. Soc.*, **88**, 2494 (1966); (b) J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Wilcott, III, *ibid.*, **89**, 4076 (1967); (c) E. Ciganek, *ibid.*, **89**, 1458 (1967); (d) V. Rautenstrauch, H. J. Scholl, and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, 7, 288 (1968); (e) L. A. Paquette, D. E. Kuhla, and J. H. Barrett, *J. Org. Chem.*, **34**, 2879 (1969).

(37) A more detailed discussion of this concept has been advanced by J. P. Freeman, D. G. Pucci, and G. Binsch, *J. Amer. Chem. Soc.*, in press.

(38) The "transfer unit" consisted of a U-tube fused at a right angle to the top of an nmr tube which was also fitted with a ₸10/30 joint for connection to the vacuum line.

the **13**-d_1 was isolated, the identical nmr spectrum was recorded with the exception that the broadened singlet at δ 4.62 now integrated for only one proton.

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Total Synthesis of Longifolene

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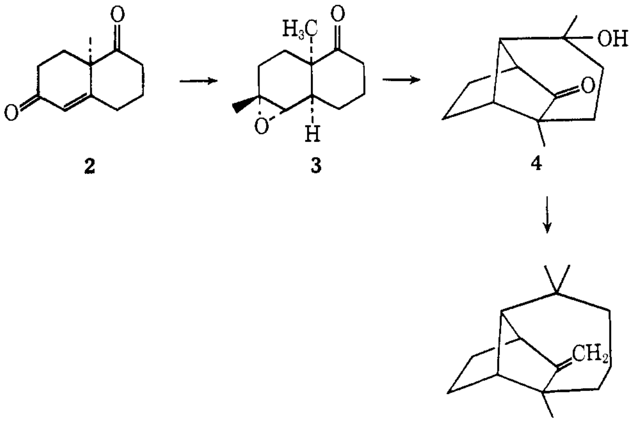
Abstract: A new route to the total synthesis of longifolene (**1**) is reported. Starting from the Wieland–Miescher ketone, the keto epoxide **10** is constructed and then cyclized by base to the tricyclic keto alcohol **11**. Dibromocarbene addition to the olefin derived from **11**, followed by silver ion assisted solvolytic ring enlargement, gives the allylic alcohol **19**. This is oxidized and treated with dimethylcopper lithium to generate ketol **23** by a surprising reductive process. Reduction of **23** to a diol followed by monomesylation and fragmentation gives dehydrolongicamphenilone (**29**) which is easily converted to longifolene.

The tricyclic sesquiterpene longifolene (**1**) is one of nature's more intricate molecular constructions and has attracted a good deal of attention in the past two decades.[1] Much of this attention has dealt with the wide variety of rearrangements which the compact longifolene skeleton undergoes, and much of it has dealt with synthesis. Thus there have been at least four unsuccessful attempts at the total synthesis of longifolene[2] as well as the well-known successful synthesis by Corey.[3] We would like to record a second total synthesis of (±)-longifolene.

Because of experience gained previously in a synthesis of the related sesquiterpene, copacamphene,[4] our attention was drawn to the possibility of forming the tricyclic carbon skeleton of longifolene *via* intramolecular alkylation of a bicyclic keto epoxide.

The Wieland–Miescher ketone (**2**) should serve as a suitable starting material to allow us to construct the necessary keto epoxide **3**. Base treatment should effect cyclization to a tricyclic compound which has sufficient functionality, properly situated, for further elaboration to longifolene.



2 **3** **4** **1**

Analogous to our synthesis of copacamphene, the Wieland–Miescher ketone was selectively monoketalized under carefully controlled conditions,[5] then hydrogenated at atmospheric pressure over a palladium catalyst to give the known[4] cis fused saturated ketone **6**, mp 54–54.5°, in approximately 85% overall yield. Treatment of **6** with methylmagnesium iodide in ether gave a crude carbinol which was dissolved in cyclohexane and stirred for 45 min at room temperature with 50% aqueous sulfuric acid to effect both dehydration and deketalization. The oily product which was obtained in 96% yield was shown by vpc to be a mixture of two compounds in the ratio 69:31. Separation was readily effected by chromatography on alumina, and the two compounds were identified as the isomeric ketones **8** and **9**. The major isomer was identified as **9** from its nmr spectrum which showed a sharp vinyl singlet at δ 5.07. It is clear from molecular models that the vinyl proton is at a dihedral angle of approximately 80° with its neighbor; thus one would expect small coupling.[6] The minor isomer **8** shows a broad vinyl absorption at δ 5.33. Equilibration experiments aimed at increasing the yield of major isomer by treatment of the mixture with toluenesulfonic acid in refluxing benzene did not change the isomer ratio.

Epoxidation of **9** with 1 equiv of *m*-chloroperbenzoic acid in chloroform at 0° gave a nearly quantitative yield of a single epoxide, mp 73–74°. Presumably this product has the desired stereochemistry as in **10**, based on analogy[4] and on the nmr spectrum which shows a sharp singlet at δ 2.55. The dihedral angle between the

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(1) (a) J. S. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, Cambridge University Press, Cambridge, England, 1952, pp 92–98; (b) G. Ourisson, *Proc. Chem. Soc.*, 274 (1964).

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(4) J. E. McMurry, *J. Org. Chem.*, **36**, 2826 (1971).

(5) J. E. McMurry, *J. Amer. Chem. Soc.*, **90**, 6821 (1968).

(6) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).