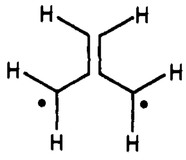
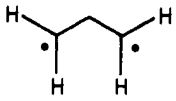
# Trimethylenemethane. Activation Energy for the Ring Closure of a 1,3 Diradical

*Sir:*

The magnitudes of the splittings among the electronic energy levels of the carbon-centered 1,3 diradicals, and the chemical and physical properties which follow, lie at the focal point of a major, current theoretical controversy. Attention is directed to the 1,3 diradicals trimethylenemethane (I)[1] and trimethylene (II),[2] and their energetic relationship to their closed-chain isomers, methylenecyclopropane and cyclopropane, respectively.



I



II

The barrier to ring closure of II to cyclopropane has been predicted, on the basis of thermodynamic and kinetic considerations, to be ∼9 kcal/mol.[3] This rather substantial barrier stands in stark contrast to the nil barrier calculated on the basis of quantum mechanical methods.[2,4] Although the disparity between the quantum mechanical and the thermodynamic-kinetic approaches has been the subject of much discussion,[2-4] the parent trimethylene diradical II being unknown as a spectroscopically detectable intermediate,[5] there has been no direct experimental test of the two conflicting predictions.

Trimethylenemethane (I) differs from II in two important respects. First, both the quantum mechanical[6] and the thermodynamic-kinetic[7] treatments are in agreement in estimating the activation barrier for the ring closure of I to methylenecyclopropane to be ∼20 kcal/mol.[7,9,10] Second, through the use of electron spin resonance spectroscopy, diradical I *is* readily observed, as a metastable intermediate.[1] Stable indefinitely at the boiling point of liquid nitrogen, trimethylenemethane (I) decays at a measureable rate at temperatures near −150 °C.[13]

The observation of rapid ring closure of diradical I at −150 °C creates some reluctance at the ready acceptance of the activation barrier of 20 kcal/mol, calculated on the basis of the theoretical models described above.[7,10,15] In addition, it appeared that examination of the experimentally accessible diradical I might illuminate some of the properties to be expected of the inaccessible diradical II. Thus, since methylenecyclopropane is characterized by a substantially more positive heat of formation,[16] reflecting in part greater strain energy,[16] than cyclopropane and since I is expected and found by its very accessibility to be more stable, relative to its transition state for ring closure, than II, the activation energy required for the ring closure of I sets an upper bound on that required for the ring closure of diradical II. Thus, it was attractive in a broad sense to determine the energy of activation for the ring closure of I, particularly so, this being the first direct observation of the kinetics of ring closure of an open-chain 1,3 diradical.

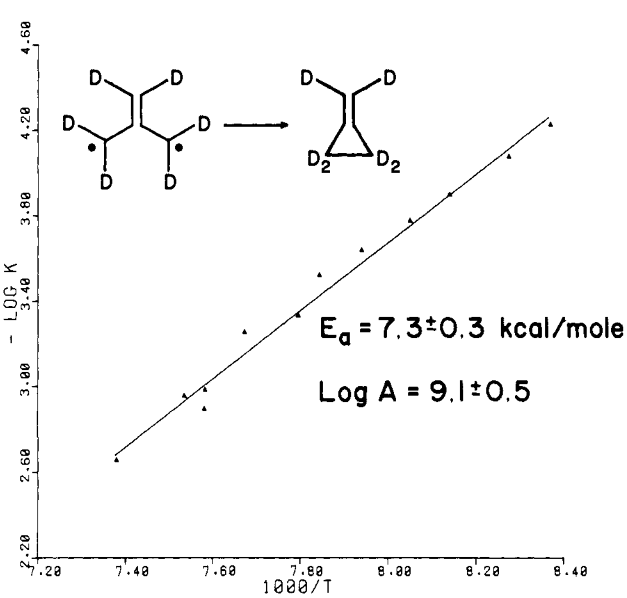


**Figure 1.** Arrhenius plot of the kinetics of ring closure of trimethylenemethane-$d_6$ (I-$d_6$) to methylenecyclopropane-$d_6$.

I was generated in frozen matrices by ultraviolet irradiation of 3-methylenecyclobutanone[17] and by $\gamma$ irradiation of methylenecyclopropane.[18] Fully deuterated trimethylenemethane (I-$d_6$) was generated by $\gamma$ irradiation of methylenecyclopropane-$d_6$. Kinetic experiments were carried out by measuring the rate of decay of the electron spin resonance spectrum of the triplet I, over the temperature range −137 to −155 °C. Good first-order kinetics were observed in all runs. The energies of activation from these several experiments are shown in Tables I and II. An Arrhenius plot leading to one of these results, that of I-$d_6$ generated by radiolysis of a neat solution of methylenecyclopropane-$d_6$, is shown in Figure 1.

**Table I.** Activation Energies for the Ring Closure of Trimethylenemethane Prepared from Methylenecyclopropane

| Starting material | $E_a$, kcal/mol[a] | Log $A$[a] | Temperature range, K |
|---|---|---|---|
| Methylenecyclopropane[b] | 7.8 ± 0.7 | 9.9 ± 1.2 | 120.1–135.0 |
| Methylenecyclopropane[c] | 7.1 ± 0.6 | 8.9 ± 0.9 | 120.7–135.0 |
| Methylenecyclopropane[d] | 6.2 ± 0.9 | 7.7 ± 1.6 | 124.2–137.1 |
| Methylenecyclopropane-$d_6$[b] | 7.3 ± 0.3 | 9.1 ± 0.5 | 119.5–135.6 |
| Methylenecyclopropane-$d_6$[e] | 7.4 ± 0.8 | 9.8 ± 1.3 | 117.7–131.9 |
| Methylenecyclopropane-$d_6$[f] | 6.6 ± 2.1 | 9.1 ± 3.9 | 112.6–122.5 |

[a] With standard deviation. [b] Neat sample. [c] 5.4 M in hexafluorobenzene. [d] 4.3 M in hexafluorobenzene. [e] 4.8 M in hexafluorobenzene. [f] 2.8 M in hexafluorobenzene.

**Table II.** Activation Energies for the Ring Closure of Trimethylenementane Prepared from 3-Methylenecyclobutanone

| Starting material | $E_a$, kcal/mol[a] | Log $A$[a] | Temperature range, K |
|---|---|---|---|
| 3-Methylenecyclobutanone[b] | 2.0 ± 0.4 | 6.7 ± 0.8 | 109.0–128.0 |
| 3-Methylenecyclobutanone[c] | 5.0 ± 0.8 | 5.8 ± 1.4 | 113.9–138.2 |
| 3-Methylenecylobutanone[d] | 3.5 ± 0.7 | 3.0 ± 1.4 | 110.6–118.1 |
| 3-Methylenecyclobutanone[e] | 4.8 ± 0.6 | 6.1 ± 1.1 | 108.1–124.2 |

[a] With standard deviation. [b] In methylenecyclopropane solvent. [c] In decalin solvent. [d] In methylcyclohexane solvent. [e] In perfluoromethylcyclohexane solvent.

Several conclusions may be drawn from the results shown in Table I. Within the limits of experimental error, no foreshortening of the activation barrier to ring closure is observed on comparing I-$d_6$ to I. Proton-tunneling apparently does not lead to truncation of the activation barrier and to a falsely low energy of activation. This is important, for the experimental activation barrier to ring closure of 7 kcal/mol is lower, by 10–20 kcal/mol, than that predicted by theory.[6,19]

Comparison of Table I and Table II shows that, while the activation energies derived from the methylenecyclopropane experiments were sensibly constant, those from 3-methylenecyclobutanone were consistently lower and more variable. This is tentatively ascribed to a possible perturbing effect of the carbon monoxide fragment. Further manifestation of some such perturbation is provided by the low and variable values of $\log A$, even in methylenecyclopropane as solvent. The low values of the energy of activation obtained from the ketone do not interfere with the main argument to be presented: that 7 kcal/mol is the maximum energy of activation for the ring closure of trimethylenemethane to methylenecyclopropane.

If the measured value of 7 kcal/mol is the maximum energy required to convert the ground-state triplet of I into the lowest singlet state of I and if it is assumed that the 41-kcal/mol activation energy for ring opening of methylenecyclopropane determined by Chesick[8] connects methylenecyclopropane ($\Delta H_f = 48$ kcal/mol)[16] with the lowest singlet state of I, then the heat of formation of ground-state triplet of I can be estimated to be $48 + 41 - 7 = 82$ kcal/mol. To the extent that activation energy is required for the conversion of the lowest singlet state of I to the triplet state of I or to methylenecyclopropane[20a] the 82-kcal/mol estimated heat of formation will be uncertain.[20b] The uncertainty is, however, bounded by the 7-kcal/mol activation energy for the triplet of I to singlet of I conversion, since this must be the highest barrier on the reaction coordinate.

It now seems reasonable, on the basis of arguments presented above, to set 7 kcal/mol as a maximum for the energy of activation of ring closure of the diradical II. It does not seem possible to go beyond this point in a rigorous fashion with the present data. However, the kinetic experiments described above do demonstrate the tendency of the thermodynamic–kinetic approach to overestimate the barrier to ring closure in a closely related diradical I. On this qualitative basis, one might suggest that diradical II probably closes to cyclopropane with an activation energy approaching that of the quantum mechanical estimates.[4]

The reason for the overestimate[7] of the thermodynamic-kinetic approach is of interest. There are two unknowns in such an estimate.[2,4c,7] One is the energy of activation for ring closure of the diradical. The other unknown is the energy required for the hypothetical cleavage of the second carbon–hydrogen bond in the thermodynamic cycle leading to the diradical. The activation energy for ring closure having been found to be substantially lower than that estimated,[7] the energy required to cleave the carbon–hydrogen bond must be considerably higher than the assumed value of 85 kcal/mol.[7] Indeed, one can make the first experimentally based estimate for the dissociation energy of the second allylic carbon–hydrogen bond in isobutylene leading to I; it is 104 kcal/mol.

The value of 7 kcal/mol, found experimentally for the energy of activation for ring closure, is of special interest as a measure of the extent of resonance stabilization afforded to the ground-state triplet of I. Simple Hückel molecular orbital theory[10] predicts an incremental resonance stabilization of 9 kcal/mol over that of the allyl radical for I. This value has as its basis the energy required for homolytic cleavage of the carbon–hydrogen bond leading to the allyl radical,[10] and would appear, thus, not to be an unreasonable estimate. It suggests a dissociation energy of 89 kcal/mol for the second allylic carbon–hydrogen bond of isobutylene. More sophisticated theoretical methods[6] have also assigned comparably substantial stabilization energies to the ground triplet state of I and, consequently, make a similar prediction for the dissociation energy of the second allylic carbon–hydrogen bond. By contrast, the value of 104 kcal/mol, derived from the experiments described here, for homolytic cleavage of the second carbon–hydrogen bond of isobutylene, leading to I, is approximately that of a normal, saturated primary carbon–hydrogen bond. This discrepancy between theory and experiment may be taken as a measure of the energetic destabilization of conjugated open-shell, 4-$\pi$-electron molecules.[21]

**Acknowledgment.** This work was generously supported by the National Science Foundation (NSF Grant No. MPS74-07864). Professor Richard Bersohn of Columbia University suggests that trimethylenemethane-$d_6$ (I-$d_6$) be examined to test the possibility that proton tunneling might intervene in the measurement of the activation energy of the ring-closure reaction.

## References and Notes

(1) (a) P. Dowd, *Acc. Chem. Res.*, **5**, 242 (1972); (b) J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, *J. Am. Chem. Soc.*, **93**, 1544 (1971).

(2) For leading references see J. A. Berson, L. D. Pedersen, and B. K. Carpenter, *J. Am. Chem. Soc.*, **98**, 122 (1976); W. von E. Doering and K. Sachdev, *ibid.*, **96**, 1168 (1974); R. G. Bergman in "Free Radicals", Vol. I, J. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 5.

(3) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961); E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).

(4) (a) R. Hoffman (*J. Am. Chem. Soc.*, **90**, 1475 (1968)) found, using the extended Hückel method, a 1-kcal/mol barrier to the ring closure of II to which, because of the approximate nature of the calculations, no special significance vis-á-vis the Benson barrier[3] was attached. (b) J. A. Horsley, Y. Jean C. Moser, L. Salem, R. M. Stevens and J. S. Wright, (*ibid.*, **94**, 279 (1972)); found no potential minimum corresponding to II in their SCF calculations and, thus, no barrier to ring closure. See also, (c) L. M. Stephenson, T. A. Gibson and J. I. Brauman, *ibid.*, **95**, 2849 (1973); (d) P. J. Hay, W. J. Hunt, and W. A. Goddard, III, *ibid.*, **94**, 638 (1972); (e) A. K. Q. Siu, W. M. St. John, III, and E. F. Hayes, *ibid.*, **92**, 7249 (1970).

(5) See, however, S. Buchwalter and G. L. Closs, *J. Am. Chem. Soc.*, **97**, 3857 (1975), who have detected 1,3-cyclopentadiyl and made a preliminary study of its decomposition at low temperature.

(6) (a) D. R. Yarkony and H. F. Schaefer, II, *J. Am. Chem. Soc.*, **96**, 3754 (1974); (b) J. H. Davis and W. A. Goddard, III, *ibid.*, **98**, 303 (1976); (c) W. J. Hehre, L. Salem, and M. R. Willcott, *ibid.*, **96**, 4328 (1974); (d) M. J. S. Dewar and J. S. Wasson, *ibid.*, **93**, 3081 (1971).

(7) The thermodynamic–kinetic cycle for trimethylenemethane may be formulated by analogy to that devised by Benson[3] for cyclopropane. If the allylic bond dissociation energies are taken as 85 kcal/mol, the heats of formation of methylenecyclopropane and isobutylene as 48 and −3 kcal/mol, respectively, and the activation energy for ring opening of methylenecyclopropane as 41 kcal/mol,[8] then the activation energy for ring closure of trimethylenemethane is predicted to be 26 kcal/mol.

(8) J. P. Chesick, *J. Am. Chem. Soc.*, **85**, 2720 (1963).

(9) The value cited is an estimate drawn from the conclusions of recent theoretical studies[6] and requires the explicit assumption that the ring-closure reaction passes through a singlet state of trimethylenemethane.

(10) Simple Hückel molecular orbital theory provides an answer comparable in magnitude with those of the more sophisticated methods above. In attempt to place such an estimate in the most appropriate context, the resonance integral $\beta$ is calculated to be 14.5 kcal/mol from $[2(2)^{1/2} - 2]\beta = 12$ kcal/mol, the resonance energy of the allyl radical.[11] Making use of this value of $\beta$, the resonance energy calculated for I is $[2(3)^{1/2} - 2]14.5 = 21.2$ kcal/mol. This is the calculated amount of energy—it being recognized that any fractional ring strain which develops is not taken into account—required in passage to a hypothetical (0,90,90) transition state geometry of I enroute to methylenecyclopropane.

(11) W. von E. Doering and G. H. Beasley, *Tetrahedron*, **29**, 2231 (1973); K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **96**, 6211 (1964). It might be argued that a value higher than 12 kcal/mol would be more appropriate when describing the activation energy required for rotation of the methylene groups out of planarity with the carbon skeleton.[12] Such an adjustment would, of course, serve only to raise the calculated barrier to ring closure.

(12) P. J. Krusic, P. Meakin, and B. E. Smart, *J. Am. Chem. Soc.*, **96**, 6211 (1974).

(13) Methylenecyclopropane is the major product of the photolytic decomposition of 3-methylenecyclobutanone, both in solution and in frozen matrices.[14]

(14) P. Dowd, G. Sengupta, and K. Sachdev, *J. Am. Chem. Soc.*, **92**, 5726 (1970). Direct observation of the formation of methylenecyclopropane, from photolysis of 3-methylenecyclobutanone at 8 K, has been made using Infrared spectrophotometry: A. Krantz, private communication.

(15) It is interesting that, although the two approaches[7,10] make distinctly dif-

ferent predictions for II, they are in essential agreement with respect to the barrier to ring closure for I.

(16) K. B. Wiberg and R. A. Fenoglio, *J. Am. Chem. Soc.*, **90**, 3395 (1968).

(17) P. Dowd and K. Sachdev, *J. Am. Chem. Soc.*, **89**, 715 (1967).

(18) K. Takeda, H. Yoshida, K. Hayashi, and S. Okamura, *Bull. Inst. Chem. Res., Kyoto Univ.*, **45**, 55 (1967); T. Yamaguchi, M. Irie, and H. Yoshida, *Chem. Lett.*, 975 (1973); H. Yoshida and O. Edlund, *Chem. Phys. Lett.*, **42**, 107 (1976).

(19) There is one apparent exception[6d] in which a MINDO/2 procedure has been used to suggest that the splitting between the (0,0,0) triplet and the (0,0,90) singlet of I is 11 kcal/mol, a value which is smaller than that calculated using other methods.[6] However, the (MINDO/2) calculations[6d] place the heat of formation of the ground-state triplet of I at 50 kcal/mol, only 2 kcal/mol higher than that of methylenecyclopropane.[16] Other conclusions of the MINDO/2 calculations have also been questioned.[6a,b]

(20) (a) This barrier may not be >7 kcal/mol. As an example, the prediction[6c] of a 9-kcal/mol barrier for the conversion of the singlet of I to methylenecyclopropane would place the singlet state below the triplet state, contrary to recent findings with regard to the multiplicity of the ground state of the molecule of I. (b) The existence of an activation barrier for the conversion of singlet of I to the triplet state of I would make the 82-kcal/mol estimate $\Delta H_f$ be too low; an activation barrier for the conversion of singlet of I to methylenecyclopropane would cause the estimated $\Delta H_f$ to be too high. Since the two possible barriers tend to cancel one another, the 82-kcal/mol estimate may be not too far from the true value.

(21) Cf. R. Breslow, *Acc. Chem. Res.*, **6**, 393 (1973), and references cited therein; M. J. S. Dewar, *Adv. Chem. Phys.*, **8**, 65 (1965); M. L. Herr, *Tetrahedron*, **32**, 2835 (1976).

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*Received February 15, 1977*

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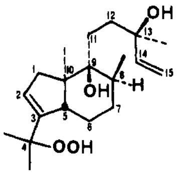
## Neoconcinndiol Hydroperoxide, a Novel Marine Diterpenoid from the Red Alga *Laurencia*

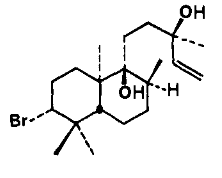
*Sir:*

The rarity of the hydroperoxide functionality in nature[1] prompts us to report here the structure of a unique diterpene hydroperoxide **1** which was isolated from extracts of the red seaweed *Laurencia snyderiae* (Dawson).[2] The structural similarity of **1** to the known diterpene concinndiol,[3] also isolated from *L. snyderiae*, prompts us to suggest the trivial name neoconcinndiol hydroperoxide for this metabolite.

Conventional silica gel column chromatography of the $CHCl_3$-MeOH (1:1) extract of the fresh algae furnished fractions, one of which (100% diethyl ether eluent) deposited crystals of **1**, $[\alpha]^{22}_D$ −35° ($c$ 0.8, $CH_3OH$), mp 158–159 °C (0.07% extract). Inspection of the earlier fractions resulted in the isolation of major amounts of **2**, mp 122–123 °C, as determined by comparisons with standard samples from *L. concinna*.[4] High resolution mass spectrometry of **1** gave major ions at $m/e$ 320.2353 for $C_{20}H_{32}O_3$ and $m/e$ 304.2404 for $C_{20}H_{32}O_2$, which reflect fragmentations of $M^+ - H_2O$ and $M^+ - H_2O, -O$, respectively, from the true molecular composition of $C_{20}H_{34}O_4$. The facile loss of water under mass spectral conditions is in complete analogy to the behavior noted earlier for **2**.[3] Initially, it appeared that **1** was an aldehyde, since a sharp one-proton singlet band was observed in the proton NMR spectrum (220 MHz, $Me_2CO$-$d_6$) at δ 9.80. The infrared spectrum of this polar compound (KBr), however, was devoid of substantial carbonyl absorption and showed, instead, intense hydroxyl absorptions. NMR $D_2O$ addition experiments showed that the sharp band at δ 9.80 and two others at δ 2.90 and 3.61 were exchangeable hydroxyl protons. The incongruity of these chemical shifts, coupled with the loss of an oxygen atom under mass spectral conditions, suggested that the δ 9.80 exchangeable band was from a hydroperoxide group.[5] Supporting this contention, **1** gave a positive iodide-iodine test for peroxides but generated complex mixtures upon attempted $NaBH_4$ reduction to the corresponding alcohol.



**1**



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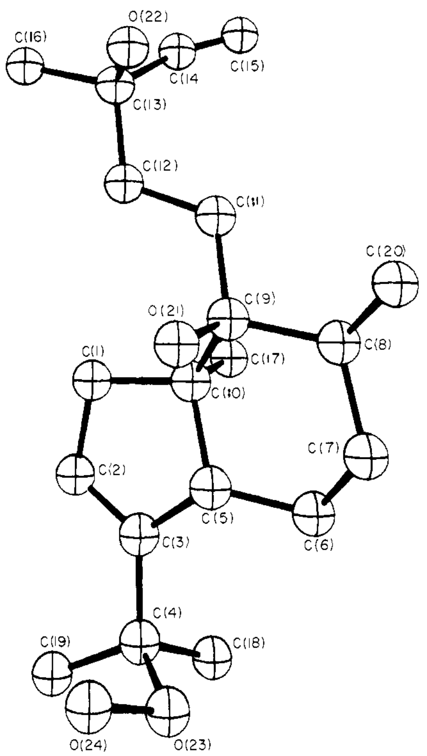

**Figure 1.** A computer generated perspective drawing of neoconcinndiol hydroperoxide. Hydrogens are omitted for clarity and only one orientation of the threefold disordered vinyl group (C(14) and C(15)) is shown.

The NMR spectrum of **1** contains a number of features which can now be assigned to structural facets of **1**. However, initially, only the relatedness to **2** could be concluded. Structural features associated with the six-carbon side chain were observed at shifts analogous to those from **2**. Specifically, the isolated vinyl group gave bands at δ 4.94 (dd, $J$ = 10, 2 Hz) and δ 5.19 (dd, $J$ = 15, 2 Hz) for the terminal protons (C(15)) and a band at δ 5.89 )dd, $J$ = 10, 15 Hz) for the C(14) olefin. Remaining in the olefin region was a single band at δ 5.43 (m), assigned to the C-2 proton, which was coupled to a set of AB double doublets (C(1) protons) at δ 3.11 and 2.61 (each $J$ = 14, 4 Hz). At high field, a six-proton singlet was observed at δ 1.29 assigned to the *gem*-dimethyl at C(4), a three-proton singlet at δ 1.22 assigned to the methyl at C(13), and, finally, a three-proton doublet at δ 0.89 ($J$ = 7 Hz) assigned to the secondary methyl at C(8).

The final structure assignment for neoconcinndiol hydroperoxide was provided by a combination of the aforementioned spectral studies with a single-crystal x-ray diffraction experiment. Preliminary x-ray photographs revealed that **1** crystallized from acetone in the monoclinic crystal class. Systematic absences conformed to space group $P2_1$ with accurate lattice constants of $a$ = 6.797 (2) Å, $b$ = 13.550 (4) Å, $c$ = 10.677 (3) Å, $\beta$ = 96.81 (3)°, and $Z$ = 2. All unique reflections with $\theta \leq$ 114.1° were measured using graphite monochromated Cu K$\alpha$ (1.541 78 Å) x rays and after Lorentz, polarization, and background corrections, 1143 (82%), were judged observed ($F_o \geq 3\sigma(F_o)$).

The structure solution proceeded with great difficulty. The largest 100 $E$'s were initially phased by hand and their values