ized *in situ* with triphenylphosphine to *cis*-stilbene.[18]

Further insight on the mechanism of this reaction can be gained from the use of optically active phosphine sulfide. Apical intramolecular nucleophilic attack at phophorus by the hydroxy group in the chiral phosphonium salt II may lead to the phosphorane I. Recent analysis by Mislow, *et al.*, on the stereochemical consequences of similar systems indicated that retention of configuration at phosphorus is expected when the phosphorus atom is incorporated in a small ring.[6] Thus, we found that (*S*)-(−)-methylphenyl-*n*-propylphosphine sulfide ($[\alpha]_D$ −5.6°),[19] on reaction with a twofold excess of cyclohexene oxide and trifluoroacetic acid, was converted to (*S*)-(−)-oxide, in greater than 89% yield, with $[\alpha]_D$ −3.8° after purification by chromatography on silica gel followed by molecular distillation. The reaction thus proceeds with retention of configuration.[20]

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(18) D. B. Denney and M. J. Boskin, *J. Amer. Chem. Soc.*, **82**, 4736 (1960); *Chem. Ind.* (*London*), 330 (1959).

(19) G. Zon, K. E. DeBruin, K. Naumann, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7023 (1969).

(20) For a facile oxidation of phosphinothioates with either retention or inversion at phosphorus, see A. W. Herriott, *ibid.*, **93**, 3304 (1971).

(21) NRCC Scholarship Recipient, 1971–1972.

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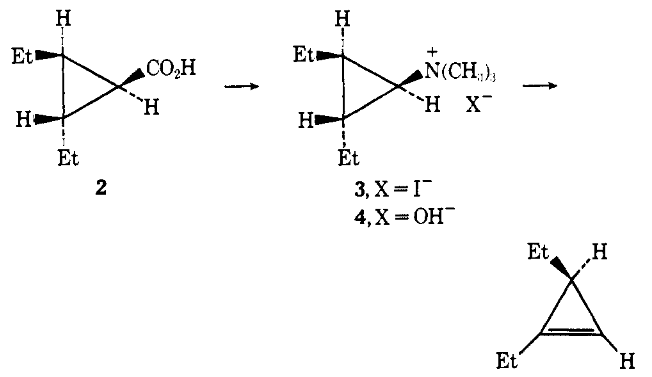
### Rapid Racemization of an Optically Active Cyclopropene Derivative *via* Ring Opening, Bond Rotation, and Ring Closure

*Sir:*

We wish to report that optically active 1,3-diethylcyclopropene (**1**) undergoes thermal racemization in the gas phase at a rate more rapid than that associated with structural isomerization. This observation indicates that despite the high strain energy (53 kcal/mol[1]) of **1**, a ring-opened species is formed on its pyrolysis which recyclizes surprisingly easily.

Synthesis and optical resolution of *trans,trans*-2,3-diethylcyclopropanecarboxylic acid (**2**, $[\alpha]^{25}_{D}$ −4.80°, $[\alpha]^{25}_{365}$ −6.45°) were performed essentially as described by Walbrick, Wilson, and Jones.[2] The acid was transformed[3] *via* acyl azide, isocyanate, methylamine, and dimethylamine to the corresponding trimethylammonium iodide **3** and thence to the quaternary hydroxide **4**. Pyrolysis (355°) of **4** in an evacuated flask containing platinized asbestos[3a] and connected to a cold trap gave optically active 1,3-diethylcyclopropene[4] (**1**, $[\alpha]^{25}_{D}$ +34.0°, $[\alpha]^{25}_{365}$ +119°) in 18% yield based on dialkylated amine (corrected for recovered amine).


**2**
**3**, X = I⁻
**4**, X = OH⁻
**1**

Thermolysis of cyclopropene **1** was carried out in a conventional well-conditioned static reactor[5] in the temperature range 160–190°. Products **5**, **6**, **7a**, and **7b** were formed[4] in essentially quantitative yield in the ratio 33:34:29:4. The first-order rate constants for total loss of optical activity ($k_\alpha$) and product formation ($k_i$) are reported in Table I.

Table I. Rate Constants and Arrhenius Parameters for Gas-Phase Thermal Racemization and Structural Isomerization of Optically Active 1,3-Diethylcyclopropene (**1**)

| Rate constants[a,b] (× 10⁵), sec⁻¹ | Temp, °C: 161.1 | Temp, °C: 175.6 | Temp, °C: 190.4 | Arrhenius parameters[c,d]: Log *A* | Arrhenius parameters[c,d]: $E_a$ |
|---|---|---|---|---|---|
| $k_\alpha$ | 2.69 | 8.04 | 29.6 | 11.8 | 32.6 |
| $k_i = k_P$ | 0.151 | 0.415 | 1.61 | 10.4 | 32.2 |
| $k_{DL}$ | 1.27 | 3.81 | 14.0 | 11.5 | 32.7 |
| $k_{DL}/k_P$ | 8.4 | 9.2 | 8.7 | | |

[a] For a definition of rate constant symbols, see the text. [b] Error limits in the reported rate constants are generally ±3%. [c] Error in log *A* is ±1 log unit; error in $E_a$ is ±1.5 kcal/mol. [d] $\Delta H^\ddagger$ (see text) calculated using the equation $\Delta H^\ddagger = E_a - nRT$ with $n = 1$ and $T = 448$ °K. Energy units are kcal/mol.

Assuming racemization does not occur by unprecedented,[6] orbital-symmetry–forbidden[7] 1,3-hydrogen shift, it must be produced by 180° rotation about the $C_1$–$C_3$ and/or $C_2$–$C_3$ bonds in **1**. We cannot rule out a completely concerted process for this motion; however, it is informative to discuss our results in terms of the formal stepwise mechanism outlined in Scheme I. Simple ring cleavage[8] in **1** could lead to "diradical" **8**. In order to produce racemization, 90° rotation must take place leading to **9**, which contains a plane of symmetry; this species is perhaps best described as a sub-

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(1) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968).

(2) J. M. Walbrick, J. W. Wilson, and W. M. Jones, *ibid.*, **90**, 2897 (1968). Drawings are not intended to reflect actual absolute configurations.

(3) (a) M. J. Schlatter, *ibid.*, **63**, 1733 (1941); (b) J. Weinstock, *J. Org. Chem.*, **26**, 3511 (1961); (c) W. H. de Wolfe and F. Bickelhaupt, *Recl. Trav. Chim. Pays-Bas*, **90**, 150 (1971).

(4) Analytical data on all new compounds reported are consistent with their assigned structures. Details of the preparative work will be reported in a full paper.

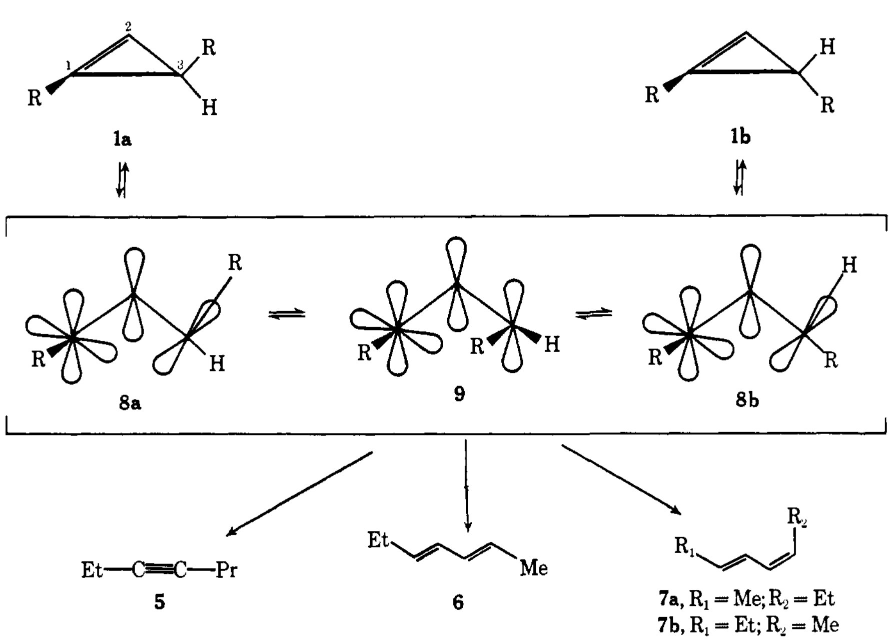
(5) Techniques used were similar to those described earlier: R. G. Bergman and W. L. Carter, *J. Amer. Chem. Soc.*, **91**, 7411 (1969).

(6) For example, 1- and 3-methylcyclopropene do *not* interconvert on pyrolysis. That 1,3-alkyl shift is not responsible for racemization is suggested by the observation that 1,3- and 3,3-dimethylcyclopropene also do not interconvert thermally: *cf.* (a) R. Srinivasan, *ibid.*, **91**, 6250 (1969); (b) R. Srinivasan, *J. Chem. Soc. D*, 1041 (1971).

(7) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970, Chapter 7.

(8) Although the $C_1$–$C_3$ bond is the most highly substituted, we believe that cleavage of both $C_1$–$C_3$ and $C_2$–$C_3$ in **1** may be occurring simultaneously (see ref 6b); racemization may therefore be the result of both processes. Our data also provide no information concerning the hybridization at $C_1$ in **9**, and the stereochemistry at $C_3$ is probably a mixture of cis and trans. For reasons of space and clarity, only one pathway is explicitly illustrated in Scheme I. The symbol X in Scheme II refers to the total set of reaction intermediates.

**Scheme I**

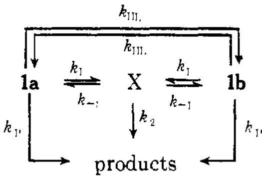


stituted "vinylcarbene."[9] Hydrogen shift in either **8** or **9** leads to acyclic products; further rotation and cyclization regenerate **1**.

Thermochemical analysis[10] predicts that the heat of formation of carbene **9** is +68 kcal/mol. That of **1** can be reliably estimated to be +42 kcal/mol,[11] and the racemization transition state is then $[\Delta H_f{}^\circ]_1 + \Delta H^{\ddagger} = +73$ kcal/mol. If one assumes that $\Delta H_f{}^\circ$ for diradical **8** is +79 kcal/mol (one allylic resonance energy[12] higher than **9**), **8** is predicted to lie *higher* in energy than the racemization transition state. It therefore seems likely that configuration **8** is stabilized by some 1,3 bonding; *i.e.*, that rotation and ring closure are synchronous processes and perhaps the only true intermediate is **9**. A quantitative estimate of the overall favorability of recyclization can be obtained by kinetic analysis of the simplified Scheme II. The unimolecular rate constants $k_{DL}$ and $k_P$ can be extracted from $k_\alpha$ and $k_i$ (Table I). Application of the steady-state assumption to the set of intermediates X shows that $[k_{DL}/k_P] = [k_{-1}/k_2]$. Our data give 8.8 as an average value for this ratio.

In summary we feel that the most reasonable intermediate for racemization of 1,3-diethylcyclopropene is a substituted vinylcarbene. Because the cyclization–hydrogen shift selectivity calculated for the set of intermediates X is only a factor of three different from that estimated[13a] for the trimethylene diradical (22), it seems unlikely that any barrier associated with ring closure has the onset of ring strain[14] as its source. Finally, the fact that vinyl diazo compounds have long been known[9] to yield cyclopropenes on thermal and photochemical decomposition suggests, in light of our observations, that such reactions proceed *via* intermediates very similar to those involved in the racemization of cyclopropene **1**.

**Scheme II**



**Acknowledgments.** We are grateful to the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society for financial support of this work and to Professor G. L. Closs for stimulating discussions.

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[9] See, for example, (a) G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 99 (1963); (b) G. L. Closs, L. E. Closs, and W. A. Boll, *ibid.*, **85**, 3796 (1963); (c) H. Dürr, *Chem. Ber.*, **103**, 369 (1970); (d) T. Severin, H. Krämer, and P. Adhikary, *ibid.*, **104**, 972 (1971); (e) M. E. Hendrick, W. J. Baron, and M. Jones, Jr., *J. Amer. Chem. Soc.*, **93**, 1554 (1971); (f) M. E. Hendrick, *ibid.*, **93**, 6337 (1971); (g) M. Franck-Neumann, *Tetrahedron Lett.*, 15 (1969); (h) G. Baum, R. Bernard, and H. Shechter, *J. Amer. Chem. Soc.*, **89**, 5307 (1967); (i) G. Büchi and J. D. White, *ibid.*, **86**, 2884 (1964); (j) G. Snatzke and H. Langen, *Chem. Ber.*, **102**, 1865 (1969); (k) L. Schrader, *ibid.*, **104**, 941 (1971); (l) G. L. Closs, L. R. Kaplan, and V. I. Bendall. *J. Amer. Chem. Soc.*, **89**, 3376 (1967); (m) 3,3-dimethylcyclopropene, on pyrolysis in olefin solution, gives a cyclopropane product which can be understood to have arisen by addition of 2-methylpropenylcarbene to the olefin; Professor G. L. Closs, private communication.

[10] The approach is that used by H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 423 (1970), and references cited therein.

[11] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

[12] Reference 11, p 215.

[13] (a) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968); (b) E. W. Schlag and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, **82**, 5996 (1960).

[14] S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

[15] (a) Alfred P. Sloan Foundation Fellow, 1970–1972; (b) Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Awardee, 1970–1975.

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## Chlorophyll–Chlorophyll Interactions. Ring V Keto Carbonyl Donor Properties from Carbon-13 Nuclear Magnetic Resonance

*Sir:*

It has become increasingly evident that the state of chlorophyll in solution is largely determined by the co-