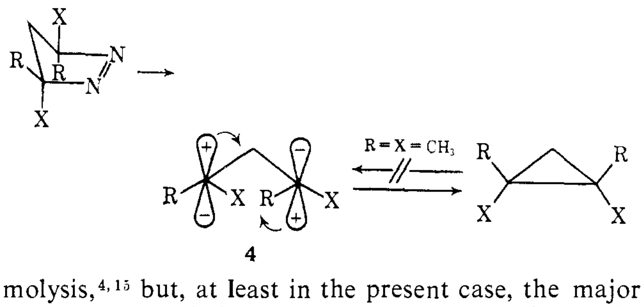
from which there is obtained hydrocarbon (**1**, R = CH_3; X = CD_3), $[\alpha]_D$ +0.41°, $[\alpha]_{365}$ +2.75° (*c* 22, isooctane). The data give the value $[\alpha]_{365}$ 3.67° for enantiomerically pure **1** (R = CH_3; X = CD_3).

The isomerization rate for this hydrocarbon in the gas phase (static system, "aged" vessel, pressure 20–50 mm) is insensitive to pressure and to surface area and obeys first-order kinetics. From measurements at five temperatures over the range 340.5–379.5°, the rate constant is expressed as $k_i = 10^{15.0}$ sec^{-1} exp((−54,400 cal/mol)/2.3*RT*).

The polarimetric rate is also first order, and at 350.2° $k_i/k_\alpha = 1.74$. This ratio may be fitted by combinations of parallel mechanisms, either 74% ($t \rightarrow c \rightarrow t$):26% ($t \rightarrow$ ri), or 87% ($t \rightarrow c \rightarrow t$):13% ($t \rightarrow t$). Among several other acceptable interpretations, a simple one involves a single type of reaction in which **1**, **3**, and **2** (R = CH_3; X = CD_3) each are cleaved reversibly between C-1 and C-2 with rate constant k_b to give separate nonplanar intermediates, **1r**, **3r**, and **2r**. These species can either recyclize with rate constant k_{cycl} or interconvert by internal bond rotations with rate constants k_{rot} for rotations **3r** → **1r** or **2r** and $2k_{rot}$ for rotations **1r** or **2r** → **3r**. The competition between internal rotation and cyclization then controls the observed rate constant ratio according to the equation $k_{cycl}/k_{rot} = 4(1 - n)/(n - 2)$, where $n = k_i/k_\alpha$. In terms of this analysis, cyclization of the intermediate is much faster than rotation about the C–C bonds, for the value $k_i/k_\alpha = 1.74$ means $k_{cycl}/k_{rot} \cong 11$. This measures the contribution of the chemically ineffective, "no-reaction" reaction by which about 11 out of 12 of the intermediates **1r** formed by cleavage of **1** merely return to it. The "true" bond-cleavage rate constant is given by $k_b = k_i/(2 - n)$.

The results show that neither a randomized intermediate (mechanism $t \rightarrow$ ri) nor an in-place rotation of one group (mechanism $t \rightarrow c \rightarrow t$) can be the sole process.[12] Further, they permit no more than a small fraction of the ring cleavages to produce *any* planar intermediate or transition state (26% if closure is random, 13% if closure is exclusively conrotatory or disrotatory). Planar diradical **4** is suggested[3, 4a] to rationalize the striking "crossover" stereochemistry of cyclopropane formation from pyrazoline thermolysis,[4, 15] but, at least in the present case, the major mode of thermal cleavage of a cyclopropane is not the microscopically reverse process. The substituted planar intermediate **4** (R = X = CH_3) probably is sterically strained relative to the unsubstituted **4** (R = X = H), and therefore a rigorous test of the possibility that conrotatory cleavage still may be preferred in cyclopropane itself awaits the application of the present technique to that molecule.



4

Acknowledgment. It is a pleasure to acknowledge the benefit of stimulating discussions with Dr. R. G. Bergman, who has kept us informed of the progress of his parallel and independent studies.

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(12) Similar conclusions have been reached regarding mechanism $t \rightarrow$ ri in the case of 1-methyl-2-ethylcyclopropane[13] and regarding mechanism $t \rightarrow c \rightarrow t$ in the case of 1,2-diphenylcyclopropane.[14]

(13) W. Carter and R. G. Bergman, *J. Am. Chem. Soc.*, 90, 7344 (1968).

(14) R. J. Crawford and T. R. Lynch, *Can. J. Chem.*, 46, 1457 (1968).

(15) For an apparent exception, see G. G. Overberger, R. E. Zangaro, and J.-P. Anselme, *J. Org. Chem.*, 31, 2046 (1966).

Optical Isomerization during the Pyrolysis of Alkylcyclopropanes. Evidence for Diradical Intermediates and an Estimate of Their Relative Rates of Bond Rotation and Ring Closure

Sir:

A great deal of information about the nature of carbon–carbon bond cleavage has been obtained in studies of the thermal isomerizations of cyclopropanes,[1–3] since these reactions are unimolecular and proceed at lower temperatures than do alkane pyrolyses. To date two types of cyclopropane thermal isomerization have been identified: (1) so-called "structural" isomerization, involving hydrogen shift and leading to propylenes, and (2) "geometrical" isomerization, which interconverts *cis–trans* isomers of substituted cyclopropanes.[1b,c] We report a study of a third type, or "optical" isomerization, which we have found interconverts enantiomers of substituted, optically active cyclopropanes at rates competitive with process 2.

Our study indicates that these isomerizations proceed through diradical intermediates rather than "π-cyclopropanes" which ring-open and -close in conrotatory fashion[4] and also provides an estimate of the relative rates of ring closure and rotation about single bonds in the diradicals.

Recrystallization of the quinine salts of both *cis*- and *trans*-2-methylcyclopropanecarboxylic acids (**1C** and **1T**)[5] from acetone, followed by treatment with aqueous hydrochloric acid, gives **1C** and **1T** in optically active form, yielding[6] predominantly (+)-(1*S*,2*R*)-**1C** and (−)-(1*R*,2*R*)-**1T**. Arndt-Eistert homologation, followed by a reduction–bromination–reduction sequence, produces optically active *cis*- and *trans*-1-methyl-2-ethylcyclopropanes ((−)-(1*R*,2*S*)-**2C** and (−)-(1*R*,2*R*)-**2T**).

Preliminary measurements of the over-all rates of racemization and geometrical isomerization of active **2T** ($[\alpha]^{25}_D$ −16.0°, 45% optically pure) and **2C** ($[\alpha]^{25}_D$

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(1) (a) T. S. Chambers and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, 56, 399 (1934); (b) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, 28, 504 (1958); (c) D. W. Setser and B. S. Rabinovitch, *J. Am. Chem. Soc.*, 86, 564 (1964); (d) H. M. Frey, *Advan. Phys. Org. Chem.*, 4, 147 (1966); (e) F. T. Smith, *J. Chem. Phys.*, 29, 235 (1958).

(2) (a) S. W. Benson, *ibid.*, 34, 521 (1961); (b) S. W. Benson and P. S. Nangia, *ibid.*, 38, 18 (1963).

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

(4) (a) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 395 (1965); (b) R. Hoffmann, *ibid.*, 90, 1475 (1968).

(5) D. E. Applequist and A. H. Peterson, *ibid.*, 82, 2372 (1960).

(6) Details of the syntheses, optical correlations, and derivations employed in this work will be presented in a full paper.

Table I. Rate Constants ($\times 10^5$) for Interconversion of Optically Active *cis*- and *trans*-1-Methyl-2-ethylcyclopropanes[a]

Temp, °C	k_r	k_r'	k_i	k_{CC}	k_{CT}	k_{TT}	k_{TC}
377.2	4.24	1.56	3.16	0.940	1.18	0.383	0.397
404.3	27.5	10.4	19.4	6.54	7.18	2.68	2.52

[a] Experimental rate constants defined as follows: k_r, over-all loss of optical activity starting with active **2C**; k_r', over-all loss of optical activity starting with active **2T**; k_i, rate of approach of racemic **2C** to the equilibrium mixture of **2C** and **2T**. Temperature constant during a run to ±0.2°; gradient across the reaction vessel <0.5°. Rate constants were determined by vpc integration and polarimetric readings at five wavelengths (Perkin-Elmer 141 polarimeter), followed by least-squares analysis employing a program written for the IBM 360/50 computer. Standard deviation in the rate constants is 1–3%.

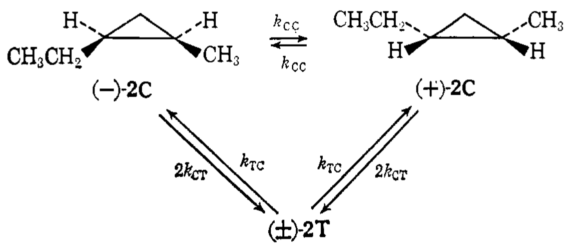
−10.13°, 62% optically pure) at 377.2 and 404.3° are reported in Table I. Kinetics were carried out in a conditioned static vessel, at pressures of 100–150 mm. Our results for the geometric isomerization correlate well with the work of Elliott and Frey[7] on the racemic series. The combined data allow calculation of E_a (57.8 kcal/mol) and log A (14.90) for the geometrical isomerization over a temperature range which has been extended 20°; these values are probably within experimental error of the earlier work.[7]

Preparative vpc separation of **2C** and **2T** from a sample of **2C** carried to about 20% conversion to **2T**

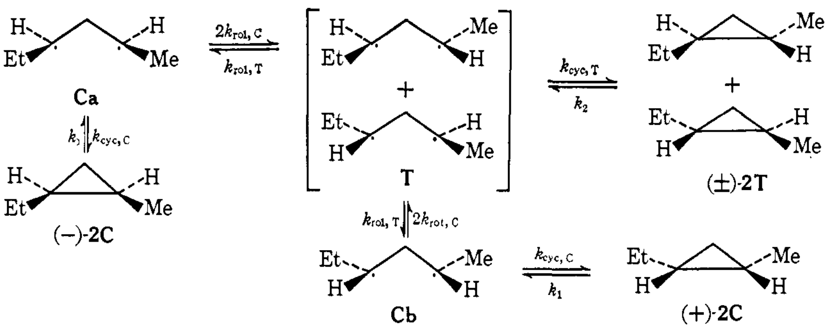
(−)-**2C** (+)-**2T**

at 377.2° gave **2T** with no detectable optical rotation at the sodium D line at concentrations used in the kinetic runs. Its rotation was, however, detectable at 365 nm, $[\alpha]^{25}_{365}$ +4° (*n*-heptane). Optical correlation of the *cis* and *trans* series of cyclopropane derivatives used in this study[6] shows that (−)-(1*R*,2*S*)-**2C** produces (+)-(1*S*,2*S*)-**2T** in the thermal isomerization with about 8% retention of optical purity.

Scheme I



Scheme II



Since this amounts to a selectivity of only 54:46 in favor of formation of (+)-**2T** over (−)-**2T** from (−)-**2C**, it is well within the experimental error of the kinetic determinations to assume that the rates of formation of (+)-**2T** and (−)-**2T** are about the same, *i.e.*, that **2T** is produced in essentially racemic form. The system is then quite accurately described as a mixture of three components ((+)-**2C**, (−)-**2C**, and (±)-**2T**) interconverting with each other by first-order processes (Scheme I). A similar scheme can be written for the system starting with active **2T**, involving rate constants k_{TT}, k_{TC}, and k_{CT}.

The differential equations for these systems are soluble in analytic form.[6] They predict that the over-all falloff in optical rotation of each system should follow a first-order rate law and allow calculation of the individual phenomenological rate constants. The values of the rate constants so determined at temperatures of 377.2 and 404.3° are listed in Table I. It is immediately apparent that the rate of interconversion of enantiomers in both the *cis* and *trans* compounds is very close to that for interconversion of geometrical isomers. There is no indication that an electrocyclic process[4] plays any significant role in the mechanism, since it would make $k_{CC} \gg k_{CT}$ and $k_{TT} \gg k_{CT}$.

While it is possible to fit the observed kinetics to a combination of independent mechanisms operating concurrently, the simplest single mechanism consistent with the data is that outlined in Scheme II.

Manipulation of the steady-state equations derived from Scheme II (and a similar scheme for the active *trans* isomer) yields relationships[6] from which relative rates of bond rotation and cyclization in the diradicals **C** and **T** can be calculated (eq 1 and 2, K = the equilibrium constant[7] for $\mathbf{2C} \rightleftharpoons \mathbf{2T}$).

$$\frac{k_{\mathrm{cyc,\,C}}}{k_{\mathrm{rot,\,C}}} = \frac{2[k_i k_r + K k_i k_r' - k_r k_r'(K + 1)]}{k_r[k_r'(K + 1) - k_i]} \qquad (1)$$

$$\frac{k_{\mathrm{cyc,\,T}}}{k_{\mathrm{rot,\,T}}} = \frac{2[k_i k_r + K k_i k_r' - k_r k_r'(K + 1)]}{k_r'[k_r(K + 1) - K k_i]} \qquad (2)$$

At 377.2°, $k_{\mathrm{cyc,\,C}}/k_{\mathrm{rot,\,C}} = 0.26$, and $k_{\mathrm{cyc,\,T}}/k_{\mathrm{rot,\,T}} = 0.29$. These values indicate that rotation is the faster process in **C** and **T** and that the rotation–ring closure selectivity is similar in both diradicals.[8]

Our results are consistent with those observed for 1,3-diphenyltrimethylene[9] and for tetramethyltrimethylene[10]

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[7] C. S. Elliott and H. M. Frey, *J. Chem. Soc.*, 900 (1964).

[8] At 404.3° the rate constants are such that it is difficult to obtain very accurate k_{cyc}/k_{rot} values (the numerator turns out to be a small difference between two large numbers), but it is clear that k_{cyc}/k_{rot} is still considerably less than 1.

[9] R. J. Crawford and T. R. Lynch, *Can. J. Chem.*, 46, 1457 (1968).

[10] J. A. Berson and J. M. Balquist, *J. Am. Chem. Soc.*, 90, 7343 (1968).

where disubstitution at each terminal carbon may well give rise to slightly higher rotational barriers and lower frequency factors for rotation,[3] making $k_{\text{cyc}} > k_{\text{rot}}$.

The intermediate or set of intermediates formed in this reaction, however, *cannot* be only the same type as those produced from the 2,5-dimethylpyrazolines,[11] despite the superficial structural similarity, since the pyrazolines apparently produce diradicals which do undergo electrocyclic closure. Models indicate that decomposition of a pyrazoline is likely to directly produce the large central bond angle intermediate predicted[4b] to undergo such closure, while this intermediate may well be inaccessible starting from a cyclopropane.

Finally (assuming that optically active **2T** isolated from the kinetic experiments is formed by tertiary–tertiary rather than secondary–tertiary bond cleavage in (−)-**2C**[12]) our optical correlation indicates that rotation is not insuperably faster than cyclization, and that rotation of a methyl-substituted carbon about a single bond is slightly more rapid than rotation of an ethyl-substituted carbon.

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[11] R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, 88, 3693 (1966). See also D. E. McGreer, N. W. K. Chiu, M. G. Vinje, and K. C. K. Wong, *Can. J. Chem.*, 43, 1407 (1965).

[12] This seems likely, based on strain considerations and the apparently general lowering of the activation energy for cyclopropane isomerizations by about 2.5–3 kcal per alkyl group. For good compilations of data, see ref 1d and 3.

[13] National Science Foundation Predoctoral Fellow, 1968–1969.

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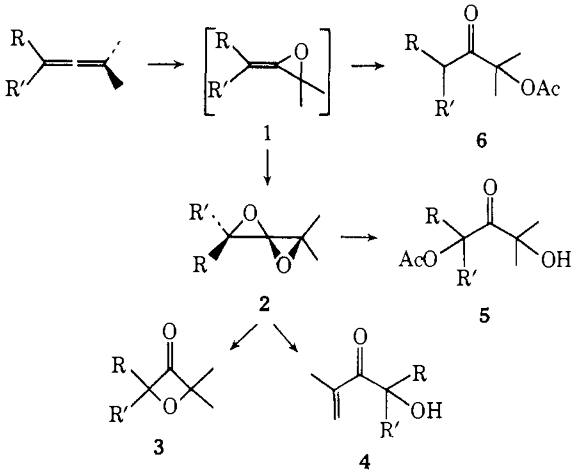
Allene Epoxidation. Isolation of a 1,4-Dioxaspiro[2.2]pentane Derivative

Sir:

We have recently postulated the existence of allene oxide **1a** and spiro dioxide **2a** as unisolated reactive intermediates in the peracid oxidation of tetramethylallene.[1] These species were invoked to provide a rational basis for the array of products (**3a**–**6a**) which was obtained from this reaction. Substantial supporting evidence for this proposal is herein presented by virtue of the isolation and characterization of 5-*t*-butyl-2,2-dimethyl-1,4-dioxaspiro[2.2]pentane (**2b**), an example of the unique spiro dioxide structure.[2] Thus, buffered peracetic acid oxidation[1] of 2,5,5-trimethyl-2,3-hexadiene[3,4] with 2 equiv of oxidant led to **2b** smoothly and in high yield. This material isomerized upon attempted glpc purification, but distillation through a spinning band column afforded a pure sample, bp 40° (2 mm). The homogeneity of this material was attested to by its well-resolved nmr spectrum: τ 6.63 (s, 1, epoxide proton), 8.54 (s, 3, CH_3), 8.56 (s, 3, CH_3), and 9.03 (s, 9, *t*-Bu). The chemical shift of the ring hydrogen is downfield about 0.5 ppm from those of simple epoxides,[5] undoubtedly owing to the effect of the neighboring oxide ring. The molecular formula of **2b** is assured by its elemental analysis (Found: C, 69.09; H, 10.18) and an accurate mass determination on the molecular ion in its mass spectrum (Found: *m/e* 156.1151).



a, R = R' = CH_3
b, R = H; R' = *t*-Bu

The mass spectrum (70 eV) showed important fragments at *m/e* (relative intensity) 156 (1), 128 (8), 113 (8), 100 (29), 98 (21), 83 (46), and 70 (100). The infrared spectrum was devoid of absorption in the hydroxyl and carbonyl regions but had a number of strong bands in the 8–14-μ region. A puzzling feature of the spectrum was the presence of a medium-intensity absorption at 6.10 μ. Interestingly, this band was absent in the Raman spectrum of **2b**.[6]

Treatment of spiro dioxide **2b** with hydrochloric acid in methylene chloride produced in good yield a 1:1 mixture of two isomeric compounds identified as oxetanone **3b** and unsaturated ketone **4b**. A variety of other acidic or thermal conditions including glpc readily effected this conversion. 4-*t*-Butyl-2,2-dimethyl-3-oxetanone (**3b**) shows: ir 5.50 μ; nmr τ 5.04 (s, 1, CH), 8.56 (s, 3, CH_3), 8.64 (s, 3, CH_3), and 9.02 (s, 9, *t*-Bu). 4-Hydroxy-2,5,5-trimethylhex-1-en-3-one

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[1] J. K. Crandall and W. H. Machleder, *Tetrahedron Lett.*, 6037 (1966); J. K. Crandall and W. H. Machleder, *J. Amer. Chem. Soc.*, 90, 7292 (1968).

[2] An early claim for this ring system has been shown to be incorrect by G. B. Hoey, D. O. Dean, and C. T. Lester, *ibid.*, 77, 391 (1955). A more recent assignment of this heterocyclic nucleus to the product from an allene epoxidation [V. I. Pansevich-Kolyada and Z. B. Idelchik, *J. Gen. Chem. USSR*, 24, 1601 (1954)] is based solely on rather poor analytical data. Our own experience leads us to severely doubt that a spiro dioxide derivative would have survived the conditions described.

[3] This allene was prepared from 2,4,4-trimethyl-2-pentene by conversion to the dibromocarbene adduct with bromoform–potassium *t*-butoxide and subsequent treatment of the adduct with methyllithium [L. Skatteb⌀l, *J. Org. Chem.*, 31, 2789 (1966)].

[4] All new compounds gave acceptable microanalytical data.

[5] For example, the methine proton in propylene oxide is found at *ca.* τ 7.1: NMR Spectra Catalog, Varian Associates, Palo Alto, Calif., 1962, Spectrum 32.

[6] This behavior appears to rule out the possibility that the absorption is C=C stretching. The nmr contraindicates the possibility of appreciable contamination by an impurity and, furthermore, the likely impurities are incompatible with the spectrum observed. The infrared band is not an overtone, but the possibility that it is an exceptionally strong combination band is not incompatible with the spectrum.