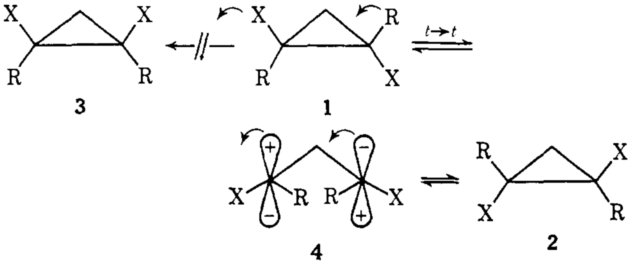
Communications to the Editor

On the Mechanism of Pyrolysis of Cyclopropanes. Racemization and Geometrical Isomerization of Tetramethylcyclopropane-d_6[1]

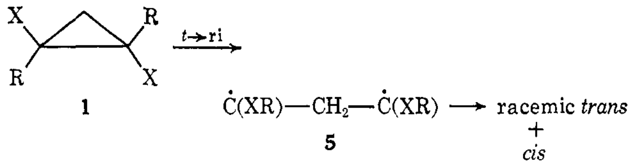
Sir:

Recent attention to the detailed mechanism of geometrical isomerization has intensified the traditional interest in pyrolysis of cyclopropanes.[2] Three extreme mechanisms may be imagined for such reactions in the case of an optically active *trans*-1,2-disubstituted cyclopropane (**1**) with like substituents (R and X) at C-1 and C-2.

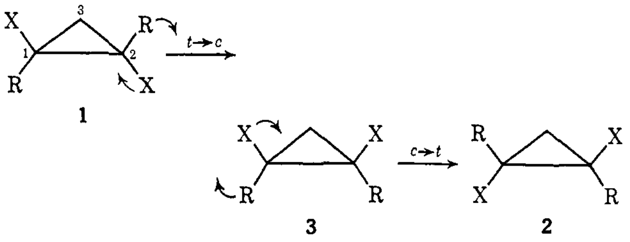
The first of these results from recent theory[3] and indirectly supporting experiment[4] which suggest that the "trimethylene diradical" often proposed[5,6] as an intermediate may be a planar species with an antisymmetric nonbonding molecular orbital (**4**) and that it may arise from and return to cyclopropane by synchronous conrotatory motions of the terminal methylene groups. (In **1**, exclusive conrotation is indistinguishable from exclusive disrotation.) If only the most heavily substituted bond breaks, this mechanism ($t \rightarrow t$) cannot form *cis* compound **3** but can only convert **1** into the enantiomeric *trans* compound **2**.



In the second possibility, bond rotations in the "trimethylene diradical" are fast relative to recyclization, as is proposed[6] for the intermediate from cyclopropane itself. This mechanism ($t \rightarrow$ ri) converts the *trans* compound **1** to an intermediate of randomized stereochemistry (**5**), which then recyclizes either to *cis* (**3**) or to racemic *trans*. The rapidly rotating intermediate **5** is stereochemically indistinguishable from a planar intermediate having the geometry of **4** but not restricted to exclusive conrotatory or disrotatory formation and closure.



The third mechanism, a generalization of that proposed by Smith,[7] involves rotation of one of the substituted carbons through 180°, converting *trans* (**1**) to *cis* (**3**), and plausibly might occur in an "expanded ring."[8] Conversion of **1** to the enantiomeric *trans* compound **2** requires *two alternating, consecutive* rotations with an obligatory pause at the *cis* compound **3** (mechanism $t \rightarrow c \rightarrow t$[9]).



For the special case where the substituents R and X are *chemically identical but actually distinguishable*, the three extreme mechanisms have simple kinetic consequences. With the polarimetric rate constant k_α for loss of optical activity in the pyrolysis of **1** defined as $\ln(\alpha_0/\alpha) = k_\alpha t$, and the isomerization rate constant k_i for approach to the *cis–trans* (C–T) equilibrium mixture (50:50) defined as $-\ln(1 - 2C/T_0) = k_i t$, the three mechanisms outlined result in experimental ratios of the rate constants as follows.

Extreme mechanism	k_i/k_α
$t \longrightarrow t$	0
$t \longrightarrow$ ri	1
$t \longrightarrow c \longrightarrow t$	2

Compounds **1** and **3** with R = CH_3 and X = CD_3 are prepared from the known[10] *trans*- and *cis*-1,2-dimethylcyclopropane-1,2-dicarboxylic acids (R = CH_3; X = CO_2H) by conversion to the diols with lithium aluminum deuteride, methanesulfonylation, and reduction again with lithium aluminum deuteride. The *trans* and *cis* isomers have virtually identical nuclear magnetic resonance (nmr) spectra, but the infrared spectra show enough differences in the fingerprint region to permit analyses of mixtures to be performed to an accuracy of 1–2%.

Optically active **1** (R = CH_3; X = CD_3; enantiomeric configuration arbitrary) is obtained from partially resolved (*via* the quinine or cinchonidine salt) *trans* acid, the enantiomeric purity of which is determined by analysis of the derived *trans* diol (**1**, R = CH_3; X = CH_2OH) by the nmr method.[11] A sample of (+) *trans* acid, 75% enantiomerically pure, is converted to the corresponding d_4 diol (**1**, R = CH_3; X = CD_2OH),

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[2] For a review, see H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 147 (1966).

[3] R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 1475 (1968).

[4] (a) R. J. Crawford and A. Mishra, *ibid.*, **87**, 3768 (1965); **88**, 3963 (1966); (b) D. E. McGreer, N. W. K. Chiu, M. G. Vinje, and K. C. K. Wong, *Can. J. Chem.*, **43**, 1407 (1965).

[5] B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

[6] (a) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968); (b) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

[7] F. T. Smith, *ibid.*, **29**, 235 (1958).

[8] E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **82**, 5996 (1960); D. W. Setser and B. S. Rabinovitch, *ibid.*, **86**, 564 (1964).

[9] Note that mechanism $t \rightarrow c \rightarrow t$ is stereochemically indistinguishable from one in which the C-2–C-3 bond breaks and rotation about C-1–C-2 in the resulting diradical is slow relative to recyclization.

[10] (a) K. von Auwers and O. Ungemach, *Ann.*, **511**, 152 (1934); (b) L. L. McCoy, *J. Am. Chem. Soc.*, **80**, 6568 (1958).

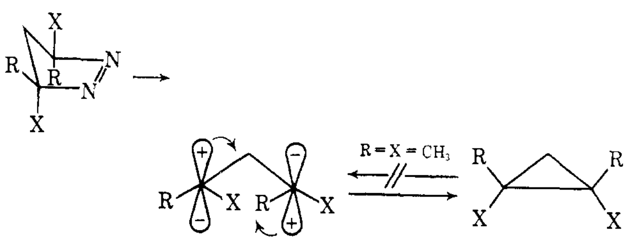
[11] M. Raban and K. Mislow, *Tetrahedron Letters*, 4249 (1965); 3961 (1966).

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 $k_i = 10^{15.0}\ \mathrm{sec}^{-1} \exp((-54{,}400\ \mathrm{cal/mol})/2.3RT)$.

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.



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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.