From these results, the maximum rotation of (+)-(1S,2R)-cyclopropanecarboxylic acid (*cis*-**8**) can be calculated to be

$$[\alpha]^{25}\mathrm{D}_{\max}(-12.0)\,\frac{(-63.1)(-77.4)}{(+44.2)(-46.4)} = +28.6^{\circ}\ \text{(ethanol)}$$

employing the value of −77.4° (ethanol) for the maximum rotation of (−)-(1R,2R)-2-methylcyclopropanecarboxylic acid (*trans* **6**).

Acknowledgments. We are indebted to Professor Robert E. Ireland for helpful discussions during the course of this work, and to the Arthur A. Noyes Fund, a du Pont Young Faculty Grant, and the Petroleum Research Fund of the American Chemical Society (Grant No 1053-G1) for financial support.

Kinetics of Racemization and *cis–trans* Isomerization of the Optically Active 1-Ethyl-2-methylcyclopropanes in the Gas Phase. An Estimate of Relative Rates of Bond Rotation and Ring Closure in Diradical Intermediates[1a]

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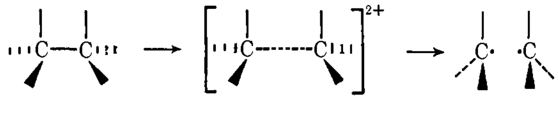
Abstract: The rates of racemization and *cis–trans* isomerization of optically active *cis*- and *trans*-1-ethyl-2-methylcyclopropane ((−)-**4C** and (−)-**4T**) have been measured at temperatures in the neighborhood of 400° in a static system in the gas phase. The rates have been analyzed to yield the unimolecular interconversion rate constants for each of the components in the system. Their similarity in magnitude indicates that an electrocyclic process proceeding through π-cyclopropane intermediates is energetically less favorable than a pathway involving stereoisomeric diradicals. A steady-state analysis of the diradical mechanism has been developed which may be solved for relative rates of rotation and cyclization of the diradicals, and these values are compared with similar numbers characteristic of diradical species which may be intermediates in other reactions already reported in the literature.



The cleavage of a carbon–carbon bond is normally assumed to occur along a reaction coordinate defined by the potential energy of the C–C stretching vibration—that is, by moving the two carbon atoms away from one another along a line coincident with the bond axis. The recent elegant discussions of carbon–carbon bond cleavage in cyclic polyolefinic systems presented by Oosterhoff,[2] Woodward and Hoffmann,[3] Longuet-Higgins and Abrahamson,[4] Fukui,[5] Zimmerman,[6] Dewar,[7] and Salem,[8] however, have suggested that this reaction can occur more easily in some cases by rotation of the two atoms with respect to one another rather than by simply moving them apart. Thus so-called "electrocyclic" bond cleavage occurs thermally in cyclic polyolefins by rotating two carbon atoms along a coordinate with σ symmetry (the disrotatory mode[3]) when there are $4n + 2$ electrons in the open-chain π system, and along a coordinate with C_2 symmetry (the conrotatory mode[3]) when there are $4n$ electrons in the open-chain π system.

The cleavage of a carbon–carbon bond which does not have an associated π-electron framework might be considered to be the simplest electrocyclic reaction. Owing to the directional nature of the orbitals making up such a bond, the three modes of bond breaking would in principle still be available, and a transient "π bond" might be an intermediate on the route to two completely free radicals. The stereochemistry of cleavage and recombination would then be controlled only by the energetic relationships of the two orbitals, modified by weak interactions with an associated σ system present in the molecule.

This paper reports the results of stereochemical investigation of such a system, the thermal cleavage, and recombination of a bond in a substituted cyclopropane.[1b] The cyclopropane molecule was selected as an object of study because its thermal reactions were known to be clean and first order, because the presence of ring strain placed temperatures necessary to induce bond cleavage in a high but still accessible region, and in order to keep the gain in entropy for dissociation of the two radical centers as low as possible. The problem can then be restated briefly as an examination of whether stereospecific ring opening and closing of a substituted cyclopropane such as **1** (by either a conrotatory or disrotatory pathway) to produce a transient "π-cyclopropane" **2** is a higher or lower energy process than direct cleavage to give a freely rotating diradical **3**.

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[1] (a) For a preliminary account of this work, see W. L. Carter and R. G. Bergman, *J. Am. Chem. Soc.*, 90, 7344 (1968); (b) National Science Foundation Predoctoral Fellow, 1968–1969.

[2] Quoted in E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, 16, 151 (1961); see also W. Th. A. M. van der Lugt and L. J. Oosterhoff, *Chem. Commun.*, 1235 (1968).

[3] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 395, 2511 (1965).

[4] H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, 87, 2045 (1965).

[5] K. Fukui, *Tetrahedron Letters*, 2009 (1965), and subsequent papers.

[6] H. E. Zimmerman, *J. Am. Chem. Soc.*, 88, 1564, 1566 (1966).

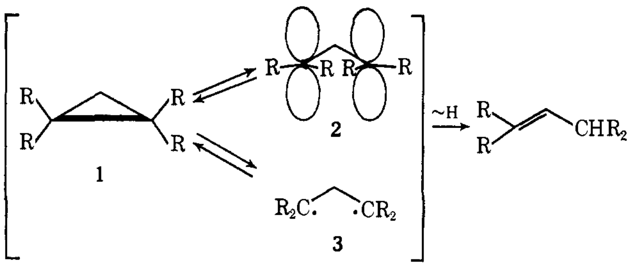
[7] M. J. S. Dewar, *Tetrahedron Suppl.*, 8, 75 (1967).

[8] L. Salem, *J. Am. Chem. Soc.*, 90, 543, 553 (1968).

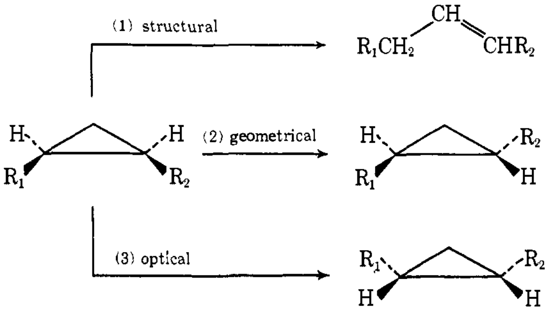
Table I. Rate Constants ($\times 10^5$) for Geometric and Optical Isomerization of *cis*- and *trans*-1-Ethyl-2-methylcyclopropanes (**4C** and **4T**)[a]

Temp, °C	k_r	k_r'	k_i	k_{CC}	k_{CT}	k_{TT}	k_{TC}
377.2	4.21	1.56	3.16	0.94	1.18	0.38	0.40
404.3	28.6	10.4	19.4	7.11	7.19	2.69	2.51
421.1	89.4	29.6	52.4	25.4	19.34	7.90	6.80
438.7	244	85.2	158	64	58	21.5	21.0

[a] For definition of rate constant symbols, see text. Standard deviation in the measured rate constants is 1-3%. Values of the equilibrium constant K for **4C** $\rightleftharpoons$ **4T** are in adequate agreement with those reported in ref 11.



Cyclopropanes have been known for some time to undergo thermal "geometric" (*cis–trans*) isomerization and "structural" isomerization to propylenes. Our approach to the problem stated above is to examine closely the rate of a third type of isomerization, which we term "optical," a process that interconverts the enantiomers of optically active 1,2-disubstituted cyclopropanes.



Experimental Section

Apparatus and Method. Thermolysis of the compounds described in this study was carried out in a conventional static gas-phase reactor of 200-ml volume. The reactor was constructed of Pyrex glass, and was joined to a Teflon stopcock by a length of capillary tubing to minimize dead space. The stopcock was then joined to a conventional vacuum line consisting of a trap, manifold, larger trap, and pump. System pressure was measured by means of a mercury manometer attached to the manifold.

The reaction flask was immersed in a 6-l. stainless steel beaker containing a molten sodium nitrite–potassium nitrate mixture.[9] The beaker was situated in the center of a large porcelain vessel and surrounded by glass wool to minimize heat loss. Also immersed in the bath was a high-speed Sargent stirrer. Heat was supplied by a 500-W base heater and a smaller 150-W knife-blade heater connected to the power source through a Bayley proportional controller (Bayley Instrument Co., Danville, Calif.). The temperature was measured by inserting an iron–constantan thermocouple into a thermocouple well built into the reactor; voltage was read on a Leeds and Northrup No. 8686 millivolt potentiometer. It was found that temperature could be routinely kept constant during a run to better than ±0.2°, and that the gradient across the reaction vessel was less than 0.5°.

The reaction vessel was conditioned by heating starting material in it at the reaction temperature for at least 24 hr before use.

Rate constants were determined by vaporizing the starting material into the reaction system (pressure in the reaction vessel during a run was always between 75 and 300 mm, well into the high-pressure region for these compounds[10]), closing the Teflon stopcock, and then removing the material after a known amount of time. The collected material was weighed and dissolved in enough *n*-heptane to make a volume of exactly 1.00 ml. The optical rotation of the solution at five wavelengths was measured on a Perkin-Elmer 141 digital readout polarimeter, and then the solution was analyzed isomerically by injection of a small amount of it onto a vapor phase chromatography (vpc) column packed with 20% Carbowax 20M on 60/80 mesh Chromosorb P. A Varian Aerograph A-90-P3 instrument was employed, along with a Honeywell recorder equipped with a Disc integrator. It was found that peak integrations could be obtained with better than 1% reproducibility.

Materials. Optically active *cis*- and *trans*-1-ethyl-2-methylcyclopropanes were prepared as described in the accompanying paper.[11] Reagent grade hydrocarbons were used to make up optical rotation solutions, and shown to have no detectable rotation at any of the five wavelengths used in this study.

Results

The rate of approach of *cis*-1-ethyl-2-methylcyclopropane (**4C**) to the equilibrium mixture of **4C** and *trans*-1-ethyl-2-methylcyclopropane (**4T**) (isomerization), as well as the rate of falloff of optical activity of the entire system starting with either optically active **4C** or **4T** could be conveniently measured in the temperature range 377.2–438.7°, were essentially uncomplicated by the much slower process of structural isomerization to olefins, and exhibited clean first-order kinetics. The rate constants for isomerization (approach to the equilibrium mixture of **4C** and **4T**) (k_i) were determined by plotting the log of the quantity $(x_e - x)/x_e$ *vs.* time, where x_e is the molar proportion of **4T** at equilibrium and x represents its proportion at any time t. An example of the type of data obtained is given in Figure 1, and rate constants for four temperatures are recorded in Table I. The **4C** $\rightleftharpoons$ **4T** equilibrium favors[10] **4T** ($K = 2.83$ at 414.1°); k_i was therefore determined starting with **4C** since this procedure yields greater precision than does the determination of k_i starting with **4T**.

The rate constants for falloff of optical activity starting with active **4C** (k_r) and **4T** (k_r') were determined by plotting the log of the quantity α_0/α where α_0 represents the initial specific optical rotation of the starting material and α represents the rotation of the mixture present at time t. An example of the type of data obtained is given in Figure 2, and the rate constants are recorded in Table I.

In all cases the rate constants and standard deviations were determined by least squares analysis of the data employing a program written for the IBM 360/50 computer. In most cases the standard deviation is from 1 to 3%. The rate data appear to agree quite well with those of Elliott and Frey,[10] who studied the rate of *cis*–

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[9] The apparatus was modified from one described by W. C. Herndon and L. L. Lowry, *J. Am. Chem. Soc.*, 86, 1922 (1964). We are grateful for suggestions about its construction provided by Professor J. A. Berson and Dr. E. J. Walsh.

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

[11] R. G. Bergman, *J. Am. Chem. Soc.*, 91, 7405 (1969).

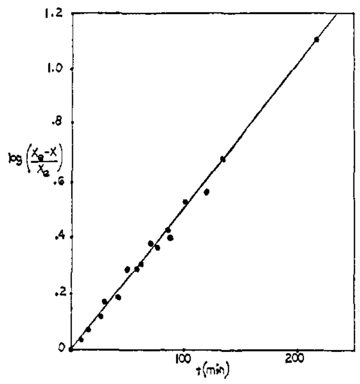


Figure 1. Variation of log $[(x_e - x)/x_e]$ with time at 404.3°, starting with *cis*-1-ethyl-2-methylcyclopropane (**4C**). Slope of the line gives $k_i = 1.94 \times 10^{-4} \pm 0.06\ \text{sec}^{-1}$

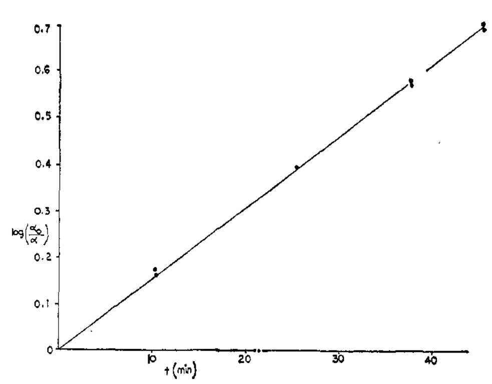
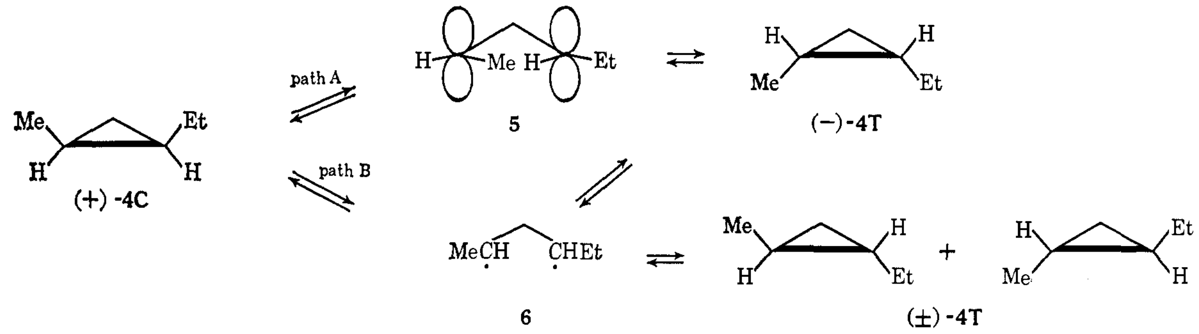


Figure 2. Variation of log (α_0/α) (see text) with time at 421.1° starting with optically active *trans*-1-ethyl-2-methylcyclopropane ((−)-**4T**). Slope of the line gives $k_r' = 2.96 \times 10^{-4} \pm 0.04\ \text{sec}^{-1}$.

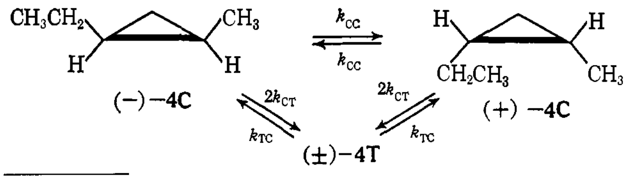
trans isomerization of racemic **4C**, and a plot of the combined data gives an activation energy of 57.8 kcal/mole, within experimental error of the previous workers' value.

Analysis of the Over-all Rate Constants. A simple inspection of the values of the rate constants provides at least an approximate answer to the problem stated in the introduction. If electrocyclic ring opening and closing of the cyclopropanes (either disrotatory or conrotatory; for simplicity only the latter process is illustrated) were a highly favored process, then the rates of racemization of **4C** and **4T** would be much greater than the rate of *cis–trans* isomerization, since the electrocyclic process retains the integrity of each geometrical isomer. In fact the rate constants k_i, k_r, and k_r' are quite similar in magnitude. Therefore the pathway leading to the π-cyclopropane (**5**) is at best only energetically competitive with that leading to some intermediate (such as **6**) which can undergo relatively rapid C–C bond rotation and thus produce *cis–trans* isomerization. In fact, the data do not *require* that **5** intervene in the mechanism at all.



In addition, the similarity in magnitude of the three rate constants also means that they are not independent, and must necessarily be made up of a combination of concurrent unimolecular processes. A completely rigorous analysis of the system involved here would have to take into account the fact that the reacting system contains four components ((+)-**4T**, (−)-**4T**, (+)-**4C**, and (−)-**4C**), each in principle capable of undergoing first-order interconversion with the other three. The analysis of such a system is extremely complex, since there are six possible pathways leading to and from each of the four components, and despite the reasonably high symmetry of the system, a total of six different unimolecular rate constants which must be extracted from the raw data. Fortunately, however, our experimental results indicate that a useful approximation can be employed. The thermolysis of (−)-**4C** was carried to about 20% conversion to its *trans* isomer, and the **4T** formed in the reaction isolated by preparative vpc. The sample of **4T** obtained in this way had no detectable optical rotation at the sodium D line, and only a very small rotation ($[\alpha]^{25}{}_{365}$ +4°) at the highest wavelength used, 365 nm. From a knowledge of the maximum rotations[11] of **4C** and **4T**, it can be calculated from this experiment that **4T** is formed from **4C** with only about 8% retention of optical purity, or better than 92% racemized.[12] It is therefore well within the experimental error of the kinetic determinations to assume that **4T** is produced in essentially racemic form. This simplifies the rate analysis considerably, because one now has to consider only a system with three interconverting components, (−)-**4C**, (+)-**4C**, and (±)-**4C**, and three rate constants k_{CC}, k_{CT}, and k_{TC}. The phenomenological scheme is shown in Scheme I. The differential equations[13] de-

Scheme I



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[12] That this is a valid mechanistic conclusion is shown by the fact that the rate of racemization of active 4T is about four times slower than the rate of racemization of 4C. Thus only a very small amount of the optical purity of 4T formed in this experiment could have been lost by racemization occurring subsequent to its formation.

[13] For convenience in writing kinetic equations, we will normally use a compound's symbol to represent its concentration; *e.g.*, in the equations, $T = [T]$, $T_{eq} = [T]_{eq}$, etc.

scribing this system are (letting L represent [(−)-**4C**], D represent [(+)-**4C**], T represent [(±)-**4T**], and $L_0 = D + L + T = \text{constant}$)

$$\frac{dL}{dt} = k_{CC}D + k_{TC}T - (2k_{TC} + k_{CC})L \tag{1}$$

$$\frac{dD}{dt} = k_{CC}L + k_{TC}T - (2k_{TC} + k_{CC})D \tag{2}$$

$$\frac{dT}{dt} = 2k_{CT}(D + L) - 2k_{TC}T \tag{3}$$

These can be solved in analytic form (see Appendix I for the general solution) to give the following concentration dependencies (employing the boundary conditions that $D_0 = T_0 = 0$).

$$T = T_{eq}(1 - e^{-2(k_{CT}+k_{TC})t}) \tag{4}$$

$$L = L_{eq} + \frac{T_{eq}}{2}e^{-2(k_{CT}+k_{TC})t} + \left(L_{eq} + \frac{T_{eq}}{2}\right)e^{-2(k_{CT}+k_{CC})t} \tag{5}$$

$$D = D_{eq} + \frac{T_{eq}}{2}e^{-2(k_{CT}+k_{TC})t} - \left(D_{eq} + \frac{T_{eq}}{2}\right)e^{-2(k_{CT}+k_{CC})t} \tag{6}$$

Now, the rate of falloff in optical rotation of the system is directly proportional to $(L - D)/L_0$. This quantity can be calculated from eq 5 and 6 and gives

$$\frac{L - D}{L_0} = e^{-2(k_{CC}+k_{CT})t} \tag{7}$$

thus confirming that racemization should be a first-order process with rate constant

$$k_r = 2(k_{CC} + k_{CT}) \tag{8}$$

Rearranging eq 4 gives

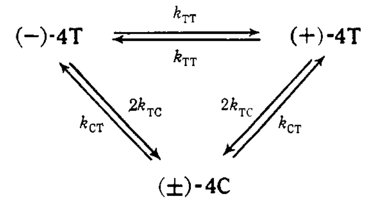
$$\frac{T_{eq} - T}{T_{eq}} = e^{-2(k_{CT}+k_{TC})t} \tag{9}$$

Thus *cis–trans* isomerization is also a first-order process with rate constant

$$k_i = 2(k_{CT} + k_{TC}) \tag{10}$$

An exactly analogous set of relationships can be derived for the racemization and isomerization of the *trans* isomer **4T**, based on Scheme II, in which the only new rate constant is k_{TT}. The rate constant for the racemization in this system is then equal to

Scheme II

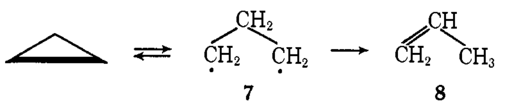


$$k_r' = 2(k_{TC} + k_{TT}). \tag{11}$$

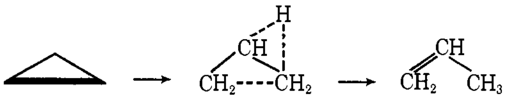
Equations 8, 10, and 11, along with the equilibrium constant $K = k_{CT}/k_{TC}$, then allow calculation of the unimolecular rate constants which describe the interconversion of each optical isomer into its enantiomer and stereoisomer. The results of these calculations are given in Table I.

Discussion

The Trimethylene Diradical. The first thorough kinetic investigation[14a] of the thermal isomerization of cyclopropane to propylene was carried out by Chambers and Kistiakowsky in 1934. Carbon–carbon bond cleavage in this system was found to be unusually facile, the isomerization taking place at a convenient high-pressure rate in the neighborhood of 450° and characterized by an activation energy of 65.0 kcal/mol and frequency factor of $10^{15.2}$. Chambers and Kistiakowsky suggested two possible mechanisms for the reaction. The first postulated an initial bond breaking to give what has come to be known as the "trimethylene diradical" (**7**); this intermediate would then undergo hydrogen shift to produce the observed product (**8**). The alternative possibility was that bond breaking and hydrogen shift occurred simultaneously to give the product in one step *via* a transition state such as **9**.



7 **8** (12)



9 **8** (13)

The clean, first-order kinetics of this isomerization, combined with the simplicity and symmetry of the cyclopropane structure, have made the reaction a frequent subject of experimental and theoretical study. Calculation of the rate constant using both Rice–Ramsberger–Kassel theory and Slater theory has been carried out,[15a–c] and though reasonable agreement with experiment has been obtained (depending on the number of vibrational oscillators assumed to be active in the isomerization), no definitive choice of mechanism has arisen from the theory.[15] O'Neal and Benson have carried out transition-state theory calculations on the individual steps of mechanism 12, estimating activation energies by thermochemical techniques and using classical harmonic oscillator and rigid-rotor approaches to calculate frequency factors. They conclude that this mechanism is most consistent with their calculations.[16] It is difficult, however, to determine which energy parameters are most reasonable for a transition state such as **9**.

Alkyl[17] and isotopic[18a–c] substitution have proven to

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[14] (a) T. S. Chambers and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, 56, 399 (1934). For a more recent study, see (b) W. E. Falconer, T. F. Hunter, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 609 (1961).

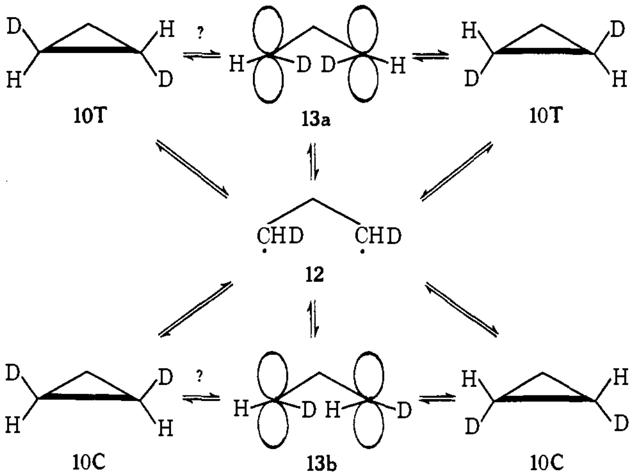
[15] (a) N. B. Slater, *Proc. Roy. Soc.* (London), **A218**, 224 (1953). See also (b) E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **82**, 5996 (1960); and (c) E. W. Schlag, Ph.D. Dissertation, University of Washington, 1958; (d) R. C. Golike and E. W. Schlag, *J. Chem. Phys.*, **38**, 1886 (1963); (e) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, pp 159–163.

[16] (a) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **71**, 2903 (1967); (b) *ibid.*, **72**, 1866 (1968); (c) S. W. Benson, "Thermochemical Kinetics," John Wiley & Sons, New York, N. Y., 1968, Chapter III. See also (d) S. W. Benson and P. S. Nangia, *J. Chem. Phys.*, **38**, 18 (1963); (e) S. W. Benson, *ibid.*, 34, 521 (1961); (f) D. W. Setser and B. S. Rabinovitch, *J. Am. Chem. Soc.*, 86, 564 (1964).

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

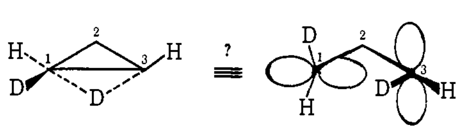
[18] (a) A. T. Blades, *Can. J. Chem.*, **39**, 1401 (1961); (b) R. E. Weston, *J. Chem. Phys.*, **26**, 975 (1957); (c) R. H. Lindquist and G. K.

be useful tools in the experimental investigation of the cyclopropane isomerization. Though no definitive decision seems to have arisen from the investigation of isotope effects on reaction rates,[15b,c,d,18a–c] a strong step forward was made when Rabinovitch, Schlag, and Wiberg[18d] demonstrated a powerful and elegant complementarity between stereochemical and kinetic techniques. These workers studied the kinetics of the thermal isomerization of *trans*-cyclopropane-d_2 (**10T**) and found that it underwent conversion to the *cis* isomer (**10C**) somewhat more rapidly than it isomerized to propylene-d_2 (**11**). This experiment demonstrates that some intermediate must exist which is capable of undergoing free rotation and reformation of starting cyclopropane, properties which one would quite normally expect of the dideuterotrimethylene diradical (**12**). The occurrence of an electrocyclic process proceeding through a π-cyclopropane (**13**) would, of course, have gone undetected in this experiment, since the compounds used were racemic and the electrocyclic process would simply have resulted in the interconversion of **10C** with itself and **10T** with itself.



10T **13a** **10T** **12** **10C** **13b** **10C**

The work of Rabinovitch, Schlag, and Wiberg[18d] stimulated Smith to suggest[19] that the geometrical isomerization might occur by a twisting of one of the CHD groups attached to one of the carbons "without ring rupture." Benson has attacked this suggestion from an energetic viewpoint,[16e] but our principal objection is in part a semantic one. The transition state visualized by Smith (**14**) must have the orbitals containing the free electrons essentially perpendicular to one another. Since these orbitals must be close to p in character, the overlap between them will be very small, and we therefor feel somewhat uncomfortable with the statement[19] that **14** has an "unruptured" ring. Smith's suggestion, however, does raise the realistic possibility that there may be some rotation of one or both of the CHD groups taking place concurrently with bond rupture (which may or may not involve increasing the spatial separation of carbons 1 and 3); *i.e*, that the two processes might be concerted.



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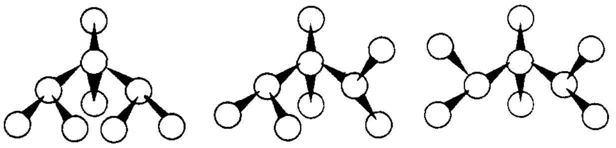
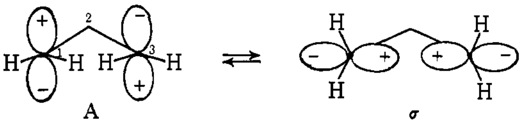
The π-Cyclopropane Problem. While our work was in progress, Hoffmann published the first extensive quantum mechanical investigation of the potential energy surfaces available to the trimethylene diradical intermediate.[20] Using extended Hückel calculations, Hoffmann investigated the total energy of the system with respect to variation of the three most important degrees of freedom of the molecule: the central CCC angle and the rotations of the terminal methylene groups out of the plane defined by the three carbon atoms. These calculations led him to the striking prediction that there should be a potential energy minimum for π-cyclopropane (his so-called 0,0 intermediate[20]) at an energy of about 1.93 eV relative to ring-closed cyclopropane, and that this intermediate should



0,0 0,90 90,90

have an energy some 4 kcal/mole or so lower than that of the "stretched" cyclopropane or 90,90 intermediate having the same central bond angle. The 0,90 intermediate—which would be the one with most similarity to Smith's[19]—was predicted to be always higher in energy than the other two, but also apparently has a subsidiary energy minimum, at a central angle of 110°.

Two properties of the 0,0 intermediate are especially worthy of note.[20] The first is that the central bond angle is calculated to be very large, *ca.* 125°. The second is that the easiest passage to and from ground-state cyclopropane is *via conrotatory* motion[2] of the terminal carbons. This is the rotational sense opposite to that predicted on the basis of simple inspection of the two half-filled orbitals. If this system could be treated as a simple two-electron, two-orbital problem, the ground state π^2 of the π-cyclopropane would correlate with the ground state σ^2 of stable cyclopropane with respect to a plane of symmetry, since both π and σ are symmetric with respect to a plane bisecting the molecule but they do not have the same symmetry with respect to a C_2 axis.[3] Thus disrotatory closure is predicted and the electrocyclic rule (disrotatory for $4n + 2$ electron systems) is preserved. The situation is apparently not so simple, however. Hoffmann explains the reversal in closure mode by pointing out[20] that the C–H orbitals at C-2 are strongly mixed into the symmetric orbital of the pseudo-π system, and this mixing results in an increase in energy of the S orbital, leaving the noninteracting antisymmetric (A) orbital as the highest occupied MO of the system. The ground states of cyclopropane and the intermediate now correlate in the C_2 mode, and conrotation is predicted.



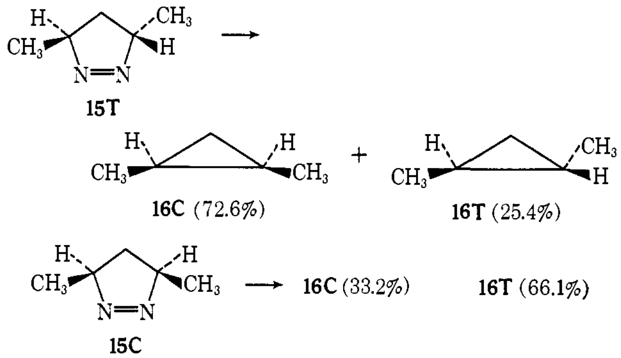
A σ

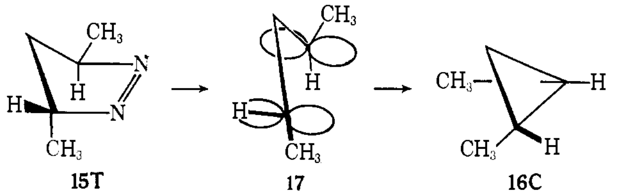
Rollefson, *J. Chem. Phys.*, **24**, 725 (1956); (d) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *ibid.*, **28**, 504 (1958). See also ref 14b,c.

(19) F. T. Smith, *J. Chem. Phys.*, **29**, 235 (1958). Schlag and Rabinovitch report[15b] that Smith has amplified his proposal to include an "expanded ring," although it is not clear whether this corresponds to "rupture" in the sense we mean it.

(20) R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 1475 (1968).

Hoffmann's calculations nicely rationalize the earlier observations of McGreer and Crawford and their coworkers,[21,22] who found that decomposition of substituted pyrazolines such as **15** produce a major amount of cyclopropanes with one net inversion of stereochemistry; *e.g.*, **15T** gives mainly **16C** and **15C** gives mainly **16T**. Crawford has carried out a number of studies which indicate that both C–N bonds break simultaneously, and therefore rationalized his results on the basis of the intermediacy of π-cyclopropanes such as **17** which prefer to close in a conrotatory sense.[22a,23]

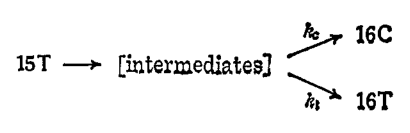


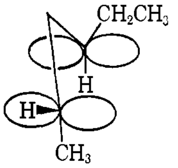


A comparison of the results of Crawford and Mishra[22a] with our work can be obtained by calculation of the selectivities of the intermediates formed in the two reactions. The pyrazoline decomposition can be considered with reference to the general reaction scheme III, where the over-all relative rate factor k_c/k_t is simply equal to the proportion of products formed. The value from **15T**, which presumably passes through intermediate **17**, is 72.6/25.4 = 2.86. The molecule in our series which should be compared with this is the *cis* isomer **4C**; if an electrocyclic mechanism were operative here, **4C** should lead to the π-cyclopropane **18**, which is very similar in structure to **17**. We must now refer to Scheme IV to calculate the selectivity of the intermediates formed in the thermal reaction of **4C**. This scheme is kinetically more complex than Scheme III, since the reverse reactions present prevent simply equating a product distribution with a selectivity factor. However, the factor of interest, k_{-2}/k_{-3}, can still be obtained. The steady-state expression for the concentration of intermediates (here called X) is

$$X = \frac{k_1L + k_2D + k_3T}{k_{-1} + k_{-2} + 2k_{-3}} \equiv \frac{k_1L + k_2D + k_3T}{\delta} \quad (14)$$

Scheme III





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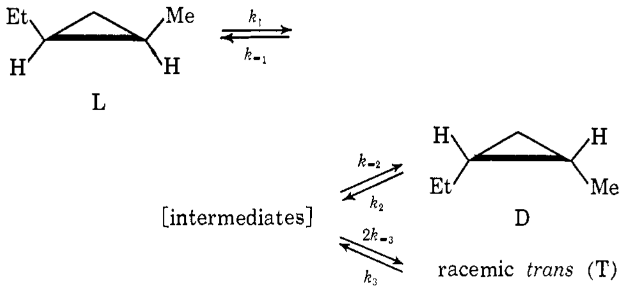
Scheme IV



For the rate dependence of D and T we have

$$\frac{dD}{dT} = k_{-2}X - k_2D = \frac{k_1k_{-2}}{\delta}L + \frac{k_2(k_{-2} - \delta)}{\delta}D + \frac{k_{-2}k_3}{\delta}T \quad (15)$$

$$\frac{dT}{dt} = 2k_{-3}X - k_3T = \frac{2k_{-3}k_1}{\delta}L + \frac{2k_{-3}k_1}{\delta}D + \frac{k_3(2k_{-3} - \delta)}{\delta}T \quad (16)$$

However, we have already written similar expressions (eq 2 and 3) with reference to the phenomenological system, Scheme I. By comparing eq 2 and 15 it must be true that

$$k_{CC} = \frac{k_1k_{-2}}{\delta} \quad (17)$$

and similarly by comparing eq 3 and 16

$$2k_{CT} = \frac{2k_{-3}k_1}{\delta} \quad (18)$$

Therefore

$$\frac{k_{-2}}{k_{-3}} = \frac{k_{CC}}{k_{CT}} \quad (19)$$

This selectivity factor for the cyclopropane pyrolysis turns out to be only 0.796 at 377.2°, compared with the pyrazoline selectivity[22a] of 2.86. The cyclopropane pyrolysis selectivity appears to deviate from this value somewhat at higher temperatures, but no clear temperature dependence emerges and the values may well be within experimental error of one another. The selectivity appears to hover about a value close to unity and in no case comes near to 2.86.

The intermediates produced in the pyrazoline decomposition therefore cannot be exactly the same as those produced in the cyclopropane pyrolysis. While no rigorous decision about the precise nature of the difference can be made at this time, it is possible to speculate about certain of the alternatives.

One possibility arises from the realization that different structural parameters must necessarily be used

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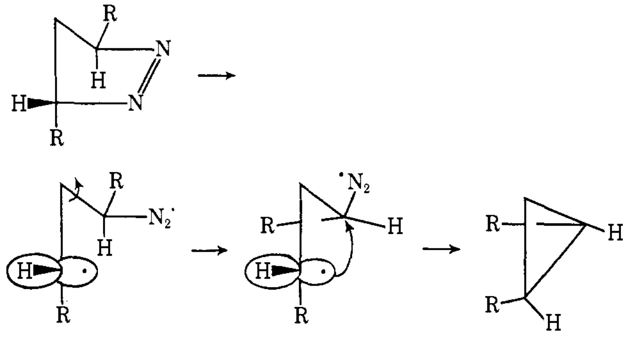
(21) (a) D. E. McGreer, R. S. McDaniel, and M. G. Vinje, *Can. J. Chem.*, 43, 1389 (1965); (b) D. E. McGreer, N. W. K. Chiu, M. G. Vinje, and K. C. K. Wong, *ibid.*, 43, 1407 (1965); (c) D. E. McGreer, N. W. K. Chiu, and M. G. Vinje, *ibid.*, 43, 1398 (1965); (d) D. E. McGreer and W.-S. Wu, *ibid.*, 45, 461 (1967).

(22) (a) R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, 88, 3963 (1966); (b) R. J. Crawford and D. M. Cameron, *ibid.*, 88, 2589 (1966); (c) R. J. Crawford and G. L. Erickson, *ibid.*, 89, 3907 (1967); (d) R. J. Crawford and L. H. Ali, *ibid.*, 89, 3908 (1967); (e) A. Mishra and R. J. Crawford, *Can. J. Chem.*, 47, 1515 (1969).

(23) B. H. Al-Sader and R. J. Crawford, *ibid.*, 46, 3302 (1968).

to describe the carbocyclic fragment present in **15** compared to those in **4**, and that one might therefore not have the right to expect the two molecules to produce intermediates with very similar structures, at least not instantaneously. One of the largest structural differences between the two precursors is the central CCC angle—in the pyrazoline it is probably somewhere near the normal tetrahedral angle of 109°, whereas in the cyclopropane it must be near 60°. Hoffmann's prediction[20] that π-cyclopropane is stable at a bond angle of 125° then suggests that this intermediate might be more accessible from **15**, where the central angle starts out large, and less accessible from **4**, which must undergo a large structural change to reach the wide-angle π-cyclopropane.[24]

A second, though somewhat less likely, possibility is that the pyrazoline decomposition does not produce a π-cyclopropane at all, but selects an alternative mechanism which also accounts for the singly inverted stereochemistry in the product. McGreer has suggested[21] that his cases might be rationalized by assuming that only one bond breaks in the initial transition state to give a zwitterion (or diradical) such as **19**. If the radical center at C-2 is now required to carry out a backside displacement of N_2 at C-4, a product of the correct stereochemistry is produced. Roth and Martin[26] have suggested a similar mechanism to explain the curious double inversion observed in the thermal decomposition of bicyclic azo compounds (*e.g.*, **20**).



19

A final possibility is that the loss of nitrogen from **15** and ring closure to give the cyclopropane are concerted. This was first considered by McGreer and coworkers.[21b] If hyperconjugation is a relatively weak phenomenon (as one might intuitively expect it to be) and the central CH_2 group does not interact significantly with the breaking bonds,[20] the nitrogen extrusion is the microscopic reverse of a hypothetical 2 + 2 cycloaddition of N_2 to a cyclopropane C–C bond. Such a reaction is predicted by the considerations of Woodward and Hoffmann to be a "${}_\sigma 2_s + {}_\sigma 2_a$" process; *i.e.*, to proceed in a suprafacial sense with respect to one of the developing fragments and an antarafacial sense with respect to the other.[27] The transition state appears to be highly strained, but perhaps can be visualized as depicted in Figure 3.

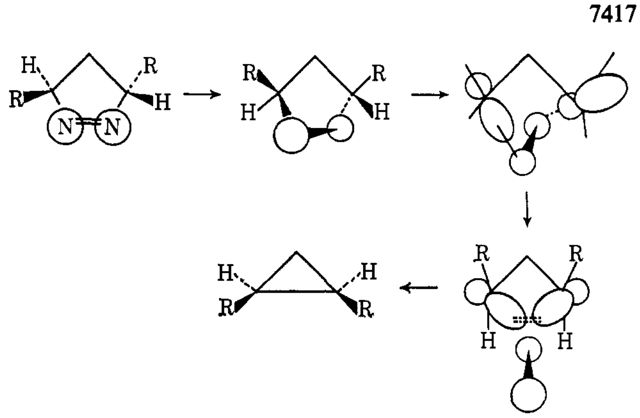
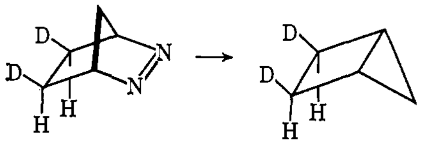


Figure 3.



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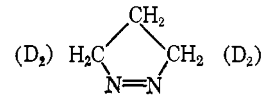
Crawford and his coworkers, on the other hand, have carried out several extensive and elegant studies that provide support for a two-step mechanism, the first concerted cleavage of both C–N bonds and the second involving reaction of a nitrogen-free three-carbon fragment.[22] The magnitude of α-deuterium isotope effects in the parent pyrazoline **21** is in good agreement with those measured by Seltzer and his coworkers in acyclic systems[23,28] where simultaneous C–N cleavage appears to be occurring. In the decomposition of 4-methyl-1-pyrazoline and its 4-*d* analog, the isotope effects are best understood in terms of the two-step mechanism.



21

Decomposition of 4-deuterio-3-methyl-1-pyrazoline gives a 50:50 yield of *cis*- and *trans*-2-deuteriomethylcyclopropane, indicating that the intermediate generated

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(24) An alternative which is difficult to discount rigorously is the possibility that the difference in selectivity is a result of the large difference in decomposition temperatures of 15 and 4, and that at 400° we simply are working at a temperature at which the two activation energy plots intersect. We have attempted to examine this by looking for a temperature dependence of k_{CC}/k_{CT}, but were frustrated by the fact that extremely accurate rate measurements would be needed to detect the small dependence expected for such a minor barrier difference at high temperatures. Another approach might be to look for a temperature dependence in the product distribution formed from 15 at lower temperatures. It should be pointed out, however, that these sorts of experiments might be inconclusive, since the temperature of the kinetic bath does not necessarily correspond to the internal "temperature" of the diradical intermediates. That is, they are almost certainly produced initially with some unknown amount of excess vibrational energy (especially in the pyrazoline decomposition, which is less endothermic than the cyclopropane pyrolysis). If the lifetime of these species is short[16d] compared to the time between collisions in the gas phase (*ca.* 10^{-11} sec), it will be difficult to know just what sort of temperature dependence, if any, to expect in the product distribution (see last section of the Discussion).

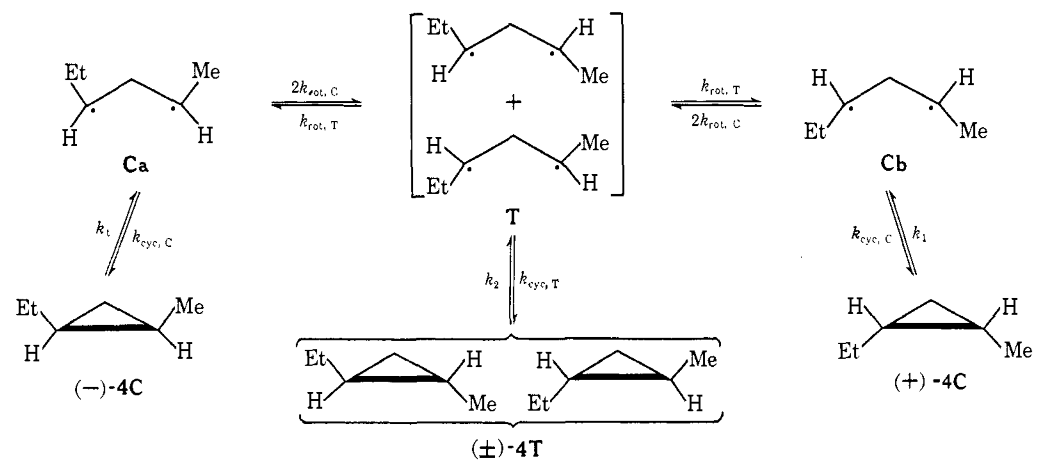
(25) (a) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, 86, 622 (1964); (b) P. D. Bartlett, C. J. Dempster, L. K. Montgomery, K. E. Schueller, and G. E. H. Wallbillich, *ibid.*, 91, 405 (1969); (c) P. D. Bartlett and G. E. H. Wallbillich, *ibid.*, 91, 409 (1969).

(26) (a) W. R. Roth and M. Martin, *Ann.*, 702, 1 (1967); (b) see also A. L. Allred and R. L. Smith, *J. Am. Chem. Soc.*, 89, 7133 (1967).

(27) (a) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968); (b) R. Hoffmann, Twelfth Conference on Reaction Mechanisms, Brandeis University, June 1968; (c) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, in press.

(28) (a) S. Seltzer and S. G. Mylonakis, *J. Am. Chem. Soc.*, 89, 6584 (1967); (b) S. Seltzer, *ibid.*, 83, 2625 (1961); (c) S. Seltzer, *ibid.*, 85, 14 (1963); (d) S. Seltzer and F. T. Dunne, *ibid.*, 87, 2628 (1965). See also (e) S. F. Nelsen and P. D. Bartlett, *ibid.*, 88, 137 (1966); (f) R. K. Lyon, *ibid.*, 86, 1907 (1964).

Scheme V



in this case has a plane of symmetry.[22c] A similar test in the *trans*-3,5-dimethyl series is provided by decomposition of optically active **15T**. *trans*-1,2-Dimethylcyclopropane (**16T**, 25% of the product) is produced with excess double inversion and 23% retention of optical purity.[22e] A dissymmetric intermediate must therefore be intervening to some extent in this system; diradical **19** fulfills the requirement of dissymmetry and will produce double inversion in the over-all reaction. The stereochemical results only *require*, however, that 6% of the total reaction proceeds *via* chiral intermediates.

In summary, though there is evidence for an electrocyclic process occurring in the pyrazoline decompositions, its intervention in the thermolysis of cyclopropanes is much more difficult to establish. For this reason, we feel that our kinetic data are most economically and usefully considered with regard to the mechanism outlined in Scheme V.

The mechanism provides a different diradical precursor for each product of the reaction, (+)-**4C**, (−)-**4C**, (+)-**4T**, and (−)-**4T** (a similar scheme can be written for the pyrolysis of optically active **4T**). This has the advantage that the rate constants in the scheme can be adjusted to provide an essentially freely rotating diradical (rotation rate constants >> cyclization rate constants) or a highly hindered diradical (cyclization rate constants >> rotation rate constants) or a spectrum of intermediate cases, each of which will produce certain values for the phenomenological rate constants, k_{CC}, k_{CT}, k_{TC}, and k_{TT}. The mechanism will not accommodate, however, a process which carries (+)-**4C** into (−)-**4C** without significant production of **4T**—for this, a separate electrocyclic mechanism must be added. It should be pointed out that the mechanism does not necessarily require the precise structure of the diradicals to be extreme forms of "stretched cyclopropanes," as shown: other conformations of the intermediates are possible (such as Smith[19] diradicals, **14**), as long as these can be assumed to be "resting places" along the energy surface which have the possibility of retaining some of their integrity after formation.

Behavior of the Diradicals. Relative Rates of Rotation and Cyclization. It is now appropriate to inquire as to the possibility of quantitatively interpreting Scheme V in terms of the observed reaction kinetics of the cyclopropane isomerization. Although the steady-state equations for Scheme V are algebraically cumbersome, *they may be solved analytically for two very important rate ratios:* $k_{cyc,C}/k_{rot,C}$, the rate of cyclization of the *cis* diradicals **Ca** and **Cb**, relative to the rate these species undergo ring closure, and $k_{cyc,T}/k_{rot,T}$, the analogous rate ratio for the *trans* diradicals **T**. An outline of the derivation is given in Appendix II; the result is that Scheme V provides a set of steady-state expressions that reduces to

$$F_c \equiv \frac{2k_{CT}}{k_{CC}} = \frac{k_{cyc,T}}{k_{rot,T}}\left(1 + \frac{2k_{rot,C}}{k_{cyc,C}}\right) \qquad (20)$$

and an analogous scheme starting from active **4T** provides a set of steady-state equations that reduces to

$$F_t \equiv \frac{2k_{TC}}{k_{TT}} = \frac{k_{cyc,C}}{k_{rot,C}}\left(1 + \frac{2k_{rot,T}}{k_{cyc,T}}\right) \qquad (21)$$

These may be treated as two equations in two unknowns; solving for the rate ratios

$$\frac{k_{cyc,C}}{k_{rot,C}} = \frac{F_cF_t - 4}{F_c + 2} \qquad (22)$$

$$\frac{k_{cyc,T}}{k_{rot,T}} = \frac{F_cF_t - 4}{F_t + 2} \qquad (23)$$

or, in terms of the measured rate constants

$$\frac{k_{cyc,C}}{k_{rot,C}} = \frac{2[k_ik_r + Kk_ik_r' - k_rk_r'(K + 1)]}{k_r[k_r'(K + 1) - k_i]} \qquad (24)$$

$$\frac{k_{cyc,T}}{k_{rot,T}} = \frac{2[k_ik_r + Kk_ik_r' - k_rk_r'(K + 1)]}{k_r'[k_r(K + 1) - Kk_i]} \qquad (25)$$

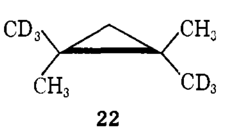
where K is the equilibrium constant relating racemic **4C** and **4T**.

A serious problem now arises in the numerical calculation of the two rate ratios. The rate and equilibrium constants shown are used repeatedly in the calculation, resulting in a serious propagation of error in the final rate ratios. In addition, the two terms on opposite sides of the minus sign in the numerator of eq 24 and 25 are large and similar in magnitude (that is, the product F_cF_t is very close to 4), and we are forced to estimate a small difference between two relatively large numbers. This propagates the error even more seriously, and so the final values of the rate ratios have a much larger percentage standard deviation (estimated by differential error analysis using a program written for the IBM

360/50 computer) than do the individual measured rate constants.

The values calculated for **C** and **T** at each temperature are essentially the same; at the four temperatures studied they are +0.3, −0.5, −0.3, and −0.1. Thus while it is impossible to pin down the $k_{\rm cyc}/k_{\rm rot}$ values very precisely, it seems clear that they are small, probably ≤ 0.3, and therefore each time a diradical is formed, it undergoes rotation to the isomeric diradical at least four or five times for each time it recyclizes to ground state cyclopropane.[29]

It is of some interest to compare the rotation–cyclization selectivity calculated for what we believe to be diradicals formed in the dialkylcyclopropane thermolysis with the selectivities exhibited for qualitatively similar intermediates generated in other systems. Berson and Balquist[30] recently examined the relative rates of racemization and *cis–trans* isomerization of optically active tetramethylcyclopropane-d_6 (**22**). Their data can also be rationalized most efficiently by invoking diradical intermediates having competitive rates of cyclization and rotation about single bonds. The mechanistic scheme is more highly symmetrical than in the methylethylcyclopropane case, since (neglecting isotope effects) the rate parameters associated with **22a** and its *cis* isomer should be identical. One therefore need make no assumptions in deriving the equations necessary to relate the rate constants for racemization and isomerization to the $k_{\rm rot}/k_{\rm cyc}$ values characteristic of **22a**; the k_i/k_r ratio for the tetramethyl system turns out to be 1.74, and this leads to a value[30] of 0.091 for $k_{\rm rot}/k_{\rm cyc}$ in **22a**.



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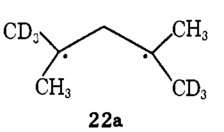
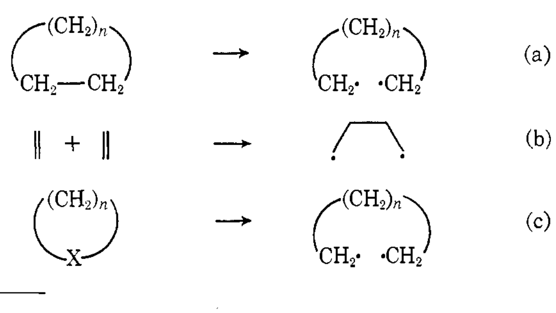


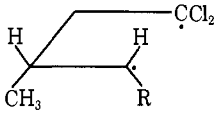
22a

A number of other diradicals—or intermediates which appear to behave very much like diradicals—have been generated, usually in one of three ways: (a) by direct cleavage of one single bond, (b) by formation of one single bond between two olefinic systems or between an olefin and carbene, and (c) by extrusion of a fragment (usually heterocyclic) from a cyclic system. Depending on the complexity of the reaction and the data available, it is often possible to calculate rotation–cyclization selectivities for the diradicals by applying the steady-state approximation to the reactive intermediates. The simplest type of system in which this can be done is the general set of pathways outlined in Scheme VI. The mechanism of some 2 + 2 cycloadditions apparently fit this scheme; this was recognized by Montgomery, Schueller, and Bartlett,[25a] who calculated k_2/k_3 and k_1/k_4 values of 12.2 and 2.63 at 100° for the diradicals **23** and **24** (where *C* represents **23** and *D* represents **24** in Scheme VI). Berson and Walsh[31] applied a similar technique to the *syn* and *anti* doubly allylic radicals **25** and **26** (formed by C–C bond cleavage in a bicyclic system), which undergo rotation and cyclization with relative rates of 0.64 and 0.086, respectively. Both Berson and Bartlett and their coworkers have suggested the difference in behavior between the two types of diradicals may arise from onset of strain in the cyclization of step **23** and **24**, as well as from the birth of some fraction of the butanediyl diradicals in conformations unfavorable to cyclization. Bartlett apparently feels that these initial radical conformations result from approach of the olefinic groups in random orientational fashion.[32]



Scheme VI

$$\begin{tikzcd}
A \arrow[r] & C \arrow[r, shift left, "k_2"] \arrow[d, "k_3"] & D \arrow[l, shift left, "k_1"] \arrow[d, "k_4"] & B \arrow[l] \\
& E & F &
\end{tikzcd}$$



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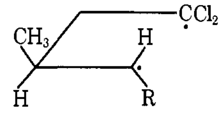

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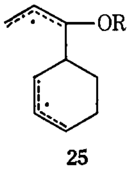

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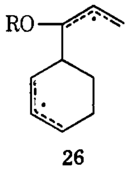
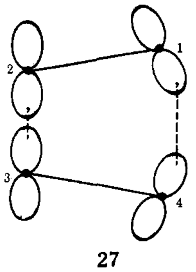


26

Simple quantum mechanical considerations, however, indicate that it may be difficult to bring two olefinic groups together in a distorted four-center orientation such as **27**—the four-center orbital arrangement will produce an antibonding interaction between the developing radical centers at C-1 and C-4. In order to avoid this antibonding interaction, the transition state will probably favor an orientation closer to **28a**, or to **28b**, an approach similar to an allowed $_\sigma2_s + {}_\sigma2_a$ transition state.[27] The kinetics will show a rate of rotation enhanced even above that of the statistical factor if the



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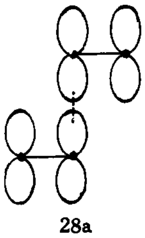
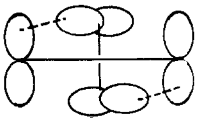


28a



28b

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[29] A kinetic phenomenon which would make F_cF_t much less than 4 would be values of $k_{\rm CC}$ and $k_{\rm TT}$ which are too large to fit the mechanism outlined in Scheme V; that is, incursion of an electrocyclic process. Unfortunately, though some of the $k_{\rm cyc}/k_{\rm rot}$ values appear to come out slightly negative, they are almost certainly within experimental error of small positive values of the rate ratios. Thus while it would be possible to fit our rate data to a composite mechanism of competing electrocyclic and diradical processes, we have chosen the more economical alternative of suggesting only one mechanism in the face of a lack of convincing data requiring the incursion of the electrocyclic process as well.

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

[31] J. A. Berson and E. J. Walsh, *ibid.*, 90, 4732 (1968).

[32] P. D. Bartlett, Reaction Mechanisms Symposium, Brandeis University, June 1968.

majority of diradicals are generated in conformations prevented from cyclizing.

Not very many other relative rates for diradical pathways are available in the literature, despite the fact that there are a number of reactions which may proceed partially or exclusively through such intermediates. The reason for this is probably the fact that besides being able to undergo rotation and cyclization, many diradicals often have at least one more pathway available to them, producing significant amounts of side products. Trimethylene-type diradicals, for example, can undergo hydrogen shift to produce olefins, and 1,4-butanediyl species like **23** and **24** might produce olefins by 2,3-bond cleavage.[25,33] This complicates the kinetics somewhat; in such cases it is necessary to represent the reaction mechanism by the general set of pathways outlined in Scheme VII. This scheme now has two additional rate constants—but it is still possible to obtain the relative rotation–cyclization ratios from a steady-state analysis of this scheme. Furthermore, the analysis also provides the rate ratios k_4/k_3 and k_5/k_6, which describe the partitioning of each diradical between cyclization and "decomposition" pathways. Letting each letter in the scheme represent the concentration of a particular component at any time, t, it must be true that

Scheme VII

$$\begin{tikzcd}
A \arrow[rr] & & C \arrow[rr, shift left, "k_2"] \arrow[dl, "k_3"'] \arrow[dr, "k_4"'] & & D \arrow[ll, shift left, "k_1"] \arrow[dl, "k_5"] \arrow[dr, "k_6"] & & B \arrow[ll] \\
& E & & F & & G &
\end{tikzcd}$$

$$\frac{\mathrm{d}F/\mathrm{d}t}{\mathrm{d}E/\mathrm{d}t} = \frac{F}{E} = \frac{k_4C + k_5D}{k_3C} = \frac{k_4}{k_3} + k_5\left(\frac{D}{k_3C}\right) \qquad (26)$$

But we also know that

$$\frac{\mathrm{d}E/\mathrm{d}t}{\mathrm{d}G/\mathrm{d}t} = \frac{E}{G} = \frac{k_3C}{k_6D} \qquad (27)$$

so

$$\frac{D}{k_3C} = \frac{G}{k_6E} \qquad (28)$$

Therefore, starting from A

$$\left[\frac{F}{E}\right]_{\mathrm{A}} = \frac{k_4}{k_3} + \frac{k_5}{k_6}\left[\frac{G}{E}\right]_{\mathrm{A}} \qquad (29)$$

and starting from B

$$\left[\frac{F}{E}\right]_{\mathrm{B}} = \frac{k_4}{k_3} + \frac{k_5}{k_6}\left[\frac{G}{E}\right]_{\mathrm{B}} \qquad (30)$$

These two equations can be solved for the two "unknowns," k_4/k_3 and k_5/k_6. Then, from the steady-state equation for the concentration of D (entering the system from A), we find

$$D = \frac{k_2C}{k_1 + k_5 + k_6} = 0 \qquad (31)$$

and

$$\left[\frac{E}{G}\right]_{\mathrm{A}} = \frac{k_3C}{k_6D} = \frac{k_3}{k_2}\left(\frac{k_1}{k_6} + \frac{k_5}{k_6} + 1\right) \qquad (32)$$

Similarly, entering the system from B, it is true that

$$\left[\frac{G}{E}\right]_{\mathrm{B}} = \frac{k_6}{k_1}\left(\frac{k_2}{k_3} + \frac{k_4}{k_3} + 1\right) \qquad (33)$$

Since k_4/k_3 and k_5/k_6 are already known, eq 32 and 33 can be solved for the two remaining unknowns, k_2/k_3 and k_1/k_6. These are the relative rates of rotation and cyclization for the diradicals C and D.

A large number of observations already in the literature can now be analyzed in terms of diradical mechanisms. Employing the above relationships derived from Scheme VII, both rotation–cyclization selectivities and cyclization–side reaction selectivities can be calculated relatively easily. Some of these values are collected in Table II. Most of the intermediates have been generated either by pyrolytic ring cleavage, thermal cycloaddition, or azo compound decomposition. A strong disclaimer should be noted with regard to the last of these processes. As discussed earlier in this paper, the mechanism of decomposition of cyclic azo compounds appears to be very difficult to generalize, and seems to be strongly altered with changes in structure such as the size and nature of the ring involved.[21,22,26] It is quite clear therefore that the pyrazoline decompositions of Crawford and Mishra,[22a] as well as the bridged pyrazoline decompositions reported by Roth and Martin and Allred and Smith,[26] will not fit the simple diradical mechanism outlined in Scheme VII unless there is some sort of inversion process taking place concurrent with nitrogen extrusion. It therefore is quite possible that varying amounts of such pathways may be competing with the diradical processes in the thermolysis of other azo compounds, such as those listed in Table II. As long as this possibility is understood, however, the reasonableness of the $k_{\mathrm{cyc}}/k_{\mathrm{rot}}$ values calculated for these presumed intermediates strongly suggests that the diradical mechanism provides an effective working hypothesis with which to discuss the mechanisms of such reactions at the present time, and we therefore feel justified in including them in the table.

Such an analysis provides an insight into the factors controlling behavior of diradical intermediates. One of the most interesting cases is that of the heterocyclic diradicals **29c** and **29t** generated photolytically from the appropriate 1,2,3-triazolenes by Scheiner.[35] The sensitized photolysis apparently proceeds through the triplet state of the diradicals, whereas the direct photolysis chooses the singlet state. Interestingly, the variation in product distribution does not require that the triplet have a greater preference for the *cis* form of the diradical or closure to *cis*-aziridine;[35] all that is required is that the $k_{\mathrm{rot}}/k_{\mathrm{cyc}}$ values for both stereoisomers increase by better than an order of magnitude in the triplet diradicals. This is quite consistent with the postulate[36] that the triplets must undergo quantum-mechanically forbidden intersystem crossing to the singlet before they recyclize, and this will tend to slow down the over-all rate of ring closure. Interestingly, the relative rates of

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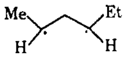
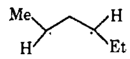
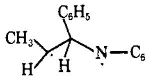
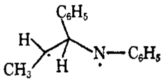
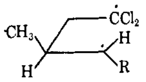
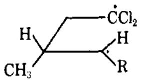
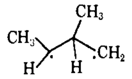
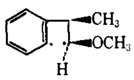
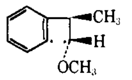
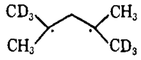
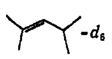
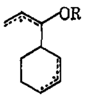
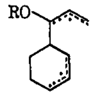
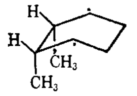
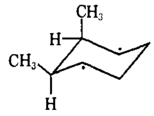
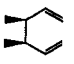
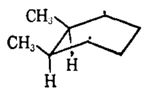
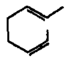
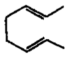
(33) Apparently **23** and **24** themselves do not undergo very much reversal to olefins, as there is very little *cis–trans* isomerization observed in the 2,4-hexadienes recovered from the reaction. Other diradicals of this type, however,[25b,c,34] yield a significant amount of olefin in the product mixture.

(34) P. D. Bartlett and N. A. Porter, *J. Am. Chem. Soc.*, 90, 5318 (1968).

(35) P. Scheiner, *ibid.*, 88, 4759 (1966).

(36) P. S. Skell and R. C. Woodworth, *ibid.*, 78, 4496 (1956).

Table II. Behavior of Possible Diradicals

Compd no.	Diradical	Method of generation	k_{rot}/k_{cyc}	k_{cyc}/k_{decomp}	Decomp product	Ref
Ca		Thermal^a	~5	Large	Olefins	This work
Cb		Thermal^a	~5	Large	Olefins	This work
29c		$h\nu$, direct^b $h\nu$, sens^b	0.43 6.7	4.0 21.8	Anil	34
29t		h , direct^b $h\nu$, sens^b	0.56 10.0	10.5 28.6	Anil	34
24		Thermal^d	2.63	Large	Olefins	25
23		Thermal^d	12.2	Large		25
31		$h\nu$, sens^e	1.86?	?	Dimethylpropenes	*h*
		Thermal^f	0.405	?	Olefin + benzyne	*i*
		Thermal^f	1.48	?		*i*
22a		Thermal^a	0.91	Very large		30
25		Thermal^g	0.64			31
26		Thermal^g	0.086			31
			k_{flip}/k_{cleave}	$k_{cleave}(t)/k_{cleave}(sec)$	$k_{cleave}(t)/k_{cleave}(sec)$	
32		Thermal^c	Very large?	?		36
33		Thermal^c	0.79	2.0		36
34		Thermal^c	15.4	2.0	 and 	36

[a] Pyrolysis of the corresponding cyclopropanes. [b] Decomposition of the appropriate 1,2,3-triazolenes. [c] Decomposition of the appropriate cyclic azo compound. [d] Cycloaddition of 1,1-dichloro-2,2-difluoroethylene and 2,4-hexadiene of indicated stereochemistry. [e] Triplet-sensitized decomposition of CH_2N_2 in the presence of *cis*-2-butene. [f] Cycloaddition of benzyne and propyl methyl ether of indicated stereochemistry. [g] Pyrolysis of the corresponding closed-ring vinyl-substituted bicyclo[2.2.1]heptene. [h] K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *J. Am. Chem. Soc.*, **83**, 2397 (1961); **84**, 1015 (1962). [i] I. Tabushi and R. Oda, *Tetrahedron Letters*, 3743 (1968); see also M. Jones, Jr., and R. H. Levin, *ibid.*, 5593 (1968); H. H. Wasserman, A. J. Solodar, and L. S. Keller, *ibid.*, 5597 (1968); L. Friedman, R. J. Osiewicz, and P. W. Rabideau, *ibid.*, 5735 (1968).

hydrogen shift and cyclization do not change by as big a factor. A similar dependence on multiplicity appears in the decomposition of the 6-ring azo compounds studied by Bartlett and Porter.[34]

Another azo compound decomposition which appears to be quite consistent with the diradical mechanism is the diazabicyclo[2.2.2]octyl system.[37] Both the boat and chair diradicals **33** and **34** undergo cleavage of the secondary–secondary bonds about half as fast as the tertiary–tertiary bonds, but the large preference for ring

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(37) W. R. Roth and M. Martin, *Tetrahedron Letters*, 3865 (1967).

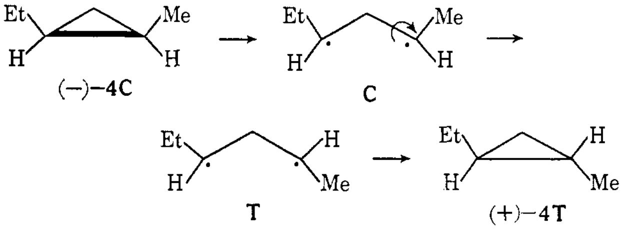
flip over cleavage in **34** testifies to its lack of stability relative to the chair conformer **33**.

As the table also indicates, substituted trimethylene diradicals appear to be intermediates in a number of reactions, and the wide differences in their behavior is at first perplexing. As pointed out earlier, the intermediates in the methylethylcyclopropane pyrolysis (**4C** and **4T**) appear to undergo rotation at least five times faster than cyclization, but the more highly substituted tetramethyltrimethylene (**22**) cyclizes about 11 times faster than it rotates.[30] Some understanding of this inversion in preference can be obtained by consideration of recent transition-state theory calculations on the rates of diradical reactions by Benson and O'Neal.[16a–c] Benson has long contended that the activation energy for recyclization must be of the order of 9 kcal/mole.[16d,e] Even though this is strictly a radical recombination, a process normally thought to proceed with essentially zero activation energy, the rather large barrier in this case is presumably due to incorporation of some cyclopropane ring strain in the transition state for ring closure. In order to estimate rates, O'Neal and Benson have developed a method of calculating the entropies of activation for these fast reactions by essentially considering the number and kind of vibrational degrees of freedom frozen out in the closure transition state. Entropies for rotation can also be calculated by treating the radical carbons and attached groups as rigid rotors, and calculating the partition functions for the rotational transition state on this basis.[16a–c] O'Neal and Benson thus calculate that the log of the frequency factor (log A) for internal rotation in the unsubstituted trimethylene diradical should be 12.9. With an estimated barrier to rotation of 3.8 kcal, trimethylene is thus predicted[16b] to have $k_{\rm rot}/k_{\rm cyc} = \sim 10$ at 750°K.

Application of these calculations to tetramethyltrimethylene, using the parameters given in ref 16b, predicts[38] a value of 2.2, whereas the observed value is 0.091. In our system $k_{\rm rot}/k_{\rm cyc}$ for the diradical **C** or **T** is predicted to be about 5. This number agrees reasonably with that calculated from our experiment. The numerical agreement in this case may well be fortuitous since there appears to be a fair amount of looseness in the estimate of energy barriers to rotation at radical centers,[16b] but we feel that at least the *trend* of the calculated values is instructive. It is clear that even if the energy barriers do not change much on substitution, placing a methyl group on the relatively low-mass methylene rotor can *decrease the frequency factor for internal rotation by as much as an order of magnitude.*

The calculations therefore emphasize the often-neglected fact that rotational entropies will be seriously affected by changes in substitution at the radical center, and may well be the determining component in the $k_{\rm rot}/k_{\rm cyc}$ decreases observed on increasing substitution.[39] It seems qualitatively reasonable then that cyclization is the fast step in **22a**, whereas rotation begins to take over in the disubstituted diradicals, and our expectation is that trimethylene itself is undoubtedly a freely rotating diradical which may have $k_{\rm rot}/k_{\rm cyc}$ much larger than the value of 10 predicted for it on the basis of O'Neal and Benson's calculations.[16]

Stereochemistry of the *cis–trans* Isomerization. An Estimate of Relative Rates of Rotation of Methyl- and Ethyl-Substituted Radical Centers. As indicated earlier in this paper, pyrolysis of (−)-**4C** to about 20% conversion to **4T** and isolation of the **4T** formed showed that it exhibited a low positive optical rotation at 365 nm ($[\alpha]^{25}{\rm D} \cong +4°$). Data from the optical correlation[10] of **4C** and **4T** can be used to determine that this corresponds to about 8% retention of optical purity in the transformation, and that (−)-*cis*-1-ethyl-2-methylcyclopropane (**4C**) of 1*S*:2*R* absolute configuration produces **4T** of 1*S*:2*S* absolute configuration in this reaction. Assuming that **4T** is formed from essentially exclusive tertiary–tertiary bond cleavage in **4C**, this means that methyl rotation in diradical C is very slightly more rapid than ethyl rotation, a result understandable on the basis of the somewhat larger mass of the ethyl rotor.



There is no *rigorous* way of ruling out the possibility of some secondary–tertiary bond cleavage occurring. However, a great deal of data in the literature on related systems indicates that such a pathway, if it occurs at all, cannot contribute greatly to the mechanism. For example, an examination of the relative activation energies for isomerization of a number of substituted cyclopropanes[41] suggests that alkyl substitution lowers these energies by about 2.5–3.0 kcal/alkyl group. Furthermore, attribution of the activity of isolated **4T** to secondary–tertiary bond breaking in **4C** would indicate that the ethyl-substituted bond breaks more slowly than the methyl-substituted bond. While structural isomerization data can be misleading, the over-all activation energy for isomerization of methylcyclopropane[42] is 65.0 kcal/mole, and for ethylcyclopropane[43] it is 61.6 kcal/mole; it would thus appear that isomerization at an ethyl center should be preferred. The effects of substituents on cyclobutane decomposition may be somewhat more reliable, since cleavage to olefins from the diradical is a faster process than isomerization and may reflect the rate of actual bond breaking more closely. The absolute magnitude of the effect is damped out somewhat, but the trend of the $E_{\rm a}$ values again indicates that a methyl-substituted bond breaks more slowly than an ethyl-substituted one.[44] These factors, combined

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(38) Private communication from Professor J. A. Berson.

(39) The rotation is undoubtedly also attenuated in **22a** by the difficulty of rotating a methyl group past the rather large disubstituted radical center.[40] This probably results in an increased rotational barrier, but a retarding entropy effect may also arise from the fact that rotation of one of the dimethyl-substituted carbon may require some restrictions on the motion of the other dimethyl-substituted carbon.[40] Diradicals **4C** and **4T** are much more similar to trimethylene in these respects, since it is possible to always carry out rotations which keep the alkyl group on the "outside" of the molecule. Complete avoidance of the "inside" rotational pathway will decrease the rotational rate at each carbon by only a statistical factor of 2.

(40) Private communication from Dr. S. W. Benson.

(41) For a good compilation of data, see ref 16b.

(42) J. P. Chesick, *J. Am. Chem. Soc.*, **82**, 3277 (1960).

(43) M. L. Halberstadt and J. P. Chesick, *J. Phys. Chem.*, **69**, 429 (1965).

(44) *Cf.* (a) C. T. Genaux, F. Kern, and W. D. Walters, *J. Am. Chem. Soc.*, **75**, 6196 (1953); (b) R. W. Carr, Jr., and W. D. Walters, *J. Phys. Chem.*, 67, 1370 (1963); (c) M. N. Das and W. D. Walters, *Z. Phys. Chem.* (Frankfurt), **15**, 23 (1958); (d) R. E. Wellmann and W. D. Walters, *J. Am. Chem. Soc.*, **79**, 1542 (1957).

with the fact that steric strain in **4C** should also favor tertiary–tertiary cleavage, provide relatively strong indications that the amount of secondary–tertiary cleavage in **4C** is probably low.

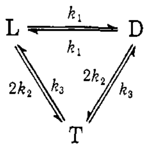
Nature of the Diradical. A number of questions concerning the structure of the diradicals produced on cyclopropane pyrolysis cannot be completely determined on the basis of our experimental data. The first of these concerns the precise positions of the rotational energy minima in these intermediates. It is conceivable that eclipsing effects are the most important destabilizing factors, in which case such a diradical might have the partially staggered form **14** as its structure of lowest energy. Even if this were the diradical's structure, however, the problem of whether **14** is the first intermediate reached in the reaction (*i.e.*, whether bond cleavage and rotation are concerted) is still a separate (and unanswered) question. The obvious problem with **14** is that rotation of one of the half-filled orbitals rapidly destroys residual bonding which may exist between the two terminal centers along the reaction coordinate leading to the diradical. It seems most reasonable to us that a cyclopropane will choose the path of lowest energy on its way to the "nonbonding" 1,3 situation, and this path is probably the one closest to the C–C vibrational stretching coordinate, since it probably retains a greater amount of overlap than does a coordinate with some rotation built into it.

The second question concerns the problem of the diradical spin multiplicity. It seems reasonable that the intermediates are in the singlet state, since there is no obvious reason for incorporation of two quantum-mechanically forbidden intersystem crossing processes into the isomerization reaction especially if (as seems most likely[20]) the diradicals have singlet ground states. Even if the diradicals have triplet ground states, one might expect the rates of intersystem crossing to be so slow as to be noncompetitive with what must be at least coenergetic singlet reaction processes. However, the data on rotation–cyclization selectivities (Table II) might at first glance be taken to provide evidence for triplet species in the cyclopropane pyrolysis. Diradicals **29c**, **29t**, **30c**, and **30t** all have $k_{\text{rot}}/k_{\text{cyc}}$ of the order of 0.1–0.5 when apparently generated as singlets; this ratio increases to 6–10 when these species are generated as triplets. The $k_{\text{rot}}/k_{\text{cyc}}$ of about 5 for diradicals **Ca** and **Cb** is closer to the triplet value. Furthermore, the very similar diradical **31**, generated[45] as a triplet by the addition of triplet methylene to *cis*-2-butene, has been estimated by Bartlett[25] to have a $k_{\text{rot}}/k_{\text{cyc}}$ value of 1.86. As we have already mentioned, however, these values are highly dependent on both structure and environment—closer examination shows that though triplet **31** generated in solution may have $k_{\text{rot}}/k_{\text{cyc}} = 1.86$, when generated in the gas phase,[46] the triplet 1,3-diradicals completely stereoequilibrate before closure occurs. Of all the diradicals in the table, **31** appears to be the most similar to **Ca** and **Cb**; the fact that $k_{\text{rot}}/k_{\text{cyc}}$ for triplet **31** generated in the gas phase must be very large therefore suggests that the singlet mechanism is still consistent with the cyclopropane pyrolysis, since **Ca** and **Cb** are also generated in the gas phase.[47]

Finally, even though these diradicals may be generated in electronic ground states, they are almost certainly produced with some quantity of excess vibrational energy, at least initially.[48] Normally the assumption is made that deactivation of any relatively complex molecule is extremely rapid,[49] and perhaps requires only one or two collisions, and thus any reactions which occur must take place by thermal reactivation of the molecule. A simple collision theory calculation, however,[50] indicates that at the pressures at which we are working, a molecule collides with another molecule in the gas phase every 10^{-11} sec or so. The calculations of O'Neal and Benson predict that a species such as the trimethylene diradical undergoes rotation at about this rate. If the calculations are only accurate to about an order of magnitude, then diradicals such as **Ca** and **Cb** might also be in the rate range in which collisional deactivation is at best only competitive with some of the processes which the diradicals undergo. A fair amount is now known about the rates of collisional activation and deactivation of simple, stable molecules.[49] The influence of activation and deactivation on the reactivity of complex molecules in relatively shallow energy minima, however, is a large area of chemistry which still remains only partially explored.

Appendix I. Generalized Derivation of Kinetic Expressions for a Completely Coupled Three-Component System of Two-fold Symmetry

For the general system



the differential equations 1, 2, and 3 can be written (see text), where $k_{\text{CC}} = k_1$, $k_{\text{CT}} = k_2$, and $k_{\text{TC}} = k_3$. Starting from pure L, $L_0 = L + D + T$. Then from eq 3

$$\frac{\mathrm{d}T}{\mathrm{d}t} = 2k_2(L_0 - T) - 2k_3T$$

$$\frac{\mathrm{d}T}{\mathrm{d}t} + 2(k_2 + k_3)T = 2k_2L_0$$

Multiplying through by $e^{2(k_2+k_3)t}$

$$\frac{\mathrm{d}T}{\mathrm{d}t}\,e^{2(k_2+k_3)t} + 2(k_2 + k_3)Te^{2(k_2+k_3)t} = 2k_2L_0e^{2(k_2+k_3)t}$$

which is equivalent to

$$\frac{\mathrm{d}}{\mathrm{d}t}\,Te^{2(k_2+k_3)t} = 2k_2L_0e^{2(k_2+k_3)t}$$

Integrating

$$Te^{2(k_2+k_3)T} = \frac{k_2L_0}{k_2 + k_3}\,e^{2(k_2+k_3)t} + K$$

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(45) See Table II, footnote *h*.

(46) (a) F. A. L. Anet, R. F. W. Bader, and A.-M. Van der Auwera, *J. Am. Chem. Soc.*, 82, 3217 (1960); see, however (b) H. M. Frey, *ibid.*, 82, 5947 (1960); (c) for a discussion of this effect, see B. S. Rabinovitch, K. W. Watkins, and D. F. Ring, *ibid.*, 87, 4960 (1965).

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(50) Reference 15e, pp 63–68.

at $t = 0, T = 0$, so

$$K = -\frac{k_2 L_0}{k_2 + k_3}$$

and

$$T = \frac{k_2 L_0}{k_2 + k_3}(1 - e^{-2(k_2+k_3)t}) = T_{eq}(1 - e^{-2(k_2+k_3)t})$$

Now, from eq 1

$$\frac{dL}{dt} = k_1(L_0 - T - L) + k_3 T - (2k_2 + k_1)L$$

$$\frac{dL}{dt} + 2(k_2 + k_1)L = k_1 L_0 + (k_3 - k_1)T_{eq} - T_{eq}(k_3 - k_1)e^{-2(k_2+k_3)t}$$

Now letting $\alpha = 2(k_1 + k_2)$, $\beta = k_1 L_0 + (k_3 - k_1)T_{eq}$, $\gamma = (k_3 - k_1)T_{eq}$, and $\delta = 2(k_2 + k_3)$

$$\frac{dL}{dt} + \alpha L = \beta - \gamma e^{-\delta t}$$

$$e^{\alpha t}\frac{d}{dt}L + \alpha L e^{\alpha t} = \beta e^{\alpha t} - \gamma e^{(\alpha-\delta)t}$$

this is equivalent to

$$\frac{d}{dt}L e^{\alpha t} = \beta e^{\alpha t} - \gamma e^{(\alpha-\delta)t}$$

Integrating

$$L e^{\alpha t} = \frac{\beta}{\alpha}e^{\alpha t} - \frac{\gamma}{(\alpha - \delta)}e^{(\alpha-\delta)t} + K$$

which, after rearrangement and substitution, gives

$$L = L_{eq} + \frac{T_{eq}}{2}e^{-\delta t} + K e^{-\alpha t}$$

At $t = 0, L = L_0$, so

$$K = Le + \frac{Te}{2}$$

and

$$L = L_{eq} + \frac{T_{eq}}{2}e^{-(2k_2+k_3)t} + \left(L_{eq} + \frac{T_{eq}}{2}\right)e^{-2(k_2+k_1)t},$$

Similarly, it can be shown that

$$D = D_{eq} + \frac{T_{eq}}{2}e^{-2(k_2+k_3)t} - \left(D_{eq} + \frac{T_{eq}}{2}\right)e^{-2(k_1+k_2)t}$$

so that

$$L - D = L_0 e^{-2(k_1+k_2)t}$$

and

$$\frac{(L + D) - (L_{eq} + D_{eq})}{T_{eq}} = e^{-2(k_2+k_3)t}$$

thus

$$k_r = 2(k_1 + k_2),\ k_i = 2(k_2 + k_3)$$

Appendix II. Derivation of k_{rot}/k_{cyc} Values for a Mechanism Involving Three Sets of Isomeric Diradicals

Consider the mechanistic scheme

From the steady-state approximation, we know that

$$Z = \frac{k_1 B + k_3 Y}{k_{-1} + k_2}$$

$$Y = \frac{k_2(X + Z) + k_5 C}{2k_3 + k_4}$$

$$X = \frac{k_1 A + k_3 Y}{k_{-1} + k_2}$$

From these equations, one derives

$$Y = \frac{k_1 k_2(A + B) + k_5(k_{-1} + k_2)C}{\delta}$$

where $\delta = 2k_{-1}k_3 + k_{-1}k_4 + k_2 k_4$. Using this expression

$$Z = \frac{\delta k_1 B + k_3 k_1 k_2(A + B) + k_3 k_5(k_{-1} + k_2)C}{\delta(k_{-1} + k_2)}$$

Therefore

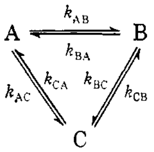
$$\frac{dB}{dt} = k_{-1}Z - k_1 B =$$

$$\frac{k_1 k_{-1} k_2 k_3 A + (k_1 k_{-1} k_2 k_3 - \delta k_1 k_2)B + k_{-1} k_3 k_5(k_{-1} + k_2)C}{\delta(k_{-1} + k_2)}$$

$$\frac{dC}{dt} = k_4 Y - k_5 C =$$

$$\frac{k_1 k_2 k_4 A + k_1 k_2 k_4 B + (k_4 k_5(k_{-1} + k_2) - \delta k_5)C}{\delta}$$

But we know from the phenomenological scheme



that

$$\frac{dB}{dt} = k_{AB}A + k_{CB}C - (k_{BA} + k_{BC})B$$

$$\frac{dC}{dt} = k_{AC}A + k_{BC}B - (k_{CA} + k_{CB})C$$

so it must be true that

$$k_{AB} = \frac{k_1 k_{-1} k_2 k_3}{\delta(k_{-1} + k_2)} \text{ and } k_{AC} = \frac{k_1 k_2 k_4}{\delta}$$

therefore

$$\frac{k_{AC}}{k_{AB}} = \frac{k_4(k_{-1} + k_2)}{k_{-1}k_3} = \frac{k_4}{k_3}\left(1 + \frac{k_2}{k_{-1}}\right)$$

Now, k_{AC}/k_{AB} can be obtained from the rate data (*cf.* Appendix I), and two equations of the above type can be obtained, one starting from active **4C** and the other from active **4T**. These can be solved for the rate ratios k_4/k_3 and k_2/k_{-1}, and the appropriate statistical factors and rate constants used in the **4C** $\rightleftharpoons$ **4T** system are employed, give eq 20–25 in the text.

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The Ethylenation of Secondary and Tertiary Alkyllithiums. II. Its Kinetics and the Nature of the Active Species

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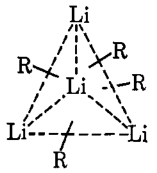
Abstract: The degree of etheration by dimethyl ether at its boiling point (−24.8°) has been measured for *n*-heptane solutions of isopropyl-, *sec*-butyl-, and *n*-butyllithium over a range of ether partial pressures. The primary alkyllithium is appreciably more strongly etherated than the secondary ones. *n*-Butyllithium approaches a limit of four ether molecules coordinated with a tetrameric organolithium aggregate. The ethylenation of isopropyl-, *sec*-butyl-, and *t*-butyllithium at −24.8° is of the first order with respect to organolithium tetramer and of the first order with respect to ethylene. With diethyl ether in 5.7- to 113-fold excess over [RLi] in *n*-pentane, the ethylenation of isopropyl- and *sec*-butyllithium is of second order in ether. With the less hindered ether, tetrahydrofuran, the rate of ethylenation of *t*-butyllithium at −40.8° in *n*-pentane passes through a maximum and later becomes inversely proportional to [THF]. Triethylamine and N-methylpyrrolidine produce a first-order catalysis of ethylenation, over a concentration range similar to that in which diethyl ether behaves in a second-order manner. 1,4-Dimethoxybutane is a strong first-order catalyst at low concentrations, but was not examined at high [ether]/[RLi] ratios. The activation parameters of the ethylenations observed lie in the range $\Delta H^{\ddagger} = 9.0\text{–}11.5$ kcal/mole and $\Delta S^{\ddagger} = -41.5$ to -25.4 eu/mole. The implications of these facts for diethyl ether catalysis are discussed in terms of a transition state (Chart I) containing one molecule of ethylene, four units of RLi, and $(2 + n)$ molecules of ether, where $n = 0$ or 1 and represents the prevalent degree of etheration over the range of conditions examined. The model predicts reaction orders which may vary with the case and the conditions. If RLi-initiated polymerization of styrene is a carbanion reaction, ethylenation is probably not one.

Alkyllithiums have long been known to exist as aggregates in hydrocarbon solvents by cryoscopic and ebullioscopic measurements.[1–4] The average molecular weight changes little or not at all with dilution. Ethyllithium has been shown to be in the form of tetrameric and hexameric aggregates in the vapor phase by mass spectroscopy.[5,6] Methyl- and ethyllithium have been shown to be tetrameric aggregates in the crystalline solid phase by X-ray crystallography.[7,8] Most recently methyl- and ethyllithium have been shown to be tetrameric in ethyl ether by ^{7}Li nmr;[9] the ^{7}Li–^{13}C coupling patterns[10] in methyllithium are in best agreement with the local-environment tetrahedral model[9] **1**.

Formula **1** shows four lithium atoms held together by electron-deficient bonding and occupying the corners of a tetrahedron. The alkyl groups are not at the corners, but on the faces, of the tetrahedron, so that each alkyl group has three lithium atoms for nearest neighbors and each lithium atom has three nearest neighbor alkyl groups. The organolithium tetramer has 16 bonding lithium orbitals and only four electron pairs. The exchange of lithium atoms in the tetrahedral aggregate is rapid compared to the transitions involved in nmr absorption at room temperature but is slower than these at −60°.[10]


1

These considerations are fundamental to any kinetic study of alkyllithium reactions. Whatever equilibrium exists between organolithium aggregates of different sizes and the organolithium monomer, any reaction of an alkyllithium will be channeled through that species for which the most favorable mechanism exists. If that species is the same as the predominant one under the reaction conditions, whatever that species may be, the reaction will appear to be of the first order with respect to alkyllithium. A reaction channeled through a higher aggregate than the prevailing one will

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