(0.1 M) in ethanol glass at 77°K had vibrational fine structure as follows: 405 nm, 0–0 band; 427, 0–1, λ_{max}; 445, 0–2; 475, 0–3; and 481 nm, 0–4 band. By use of a Tektronix 564B Storage oscilloscope equipped with a polaroid camera, the mean phosphorescent lifetime was 205 msec with excitation at 300 nm (near the n–π^* λ_{max}). Similarly, the phosphorescence spectra of 3-ethylidene-2,2,5,5-tetramethylcyclohexanone (15% E:85% Z, 0.1 M) in ethanol and isopentane glasses were recorded at 77°K. In both solvents spectra were diffuse, making the following band assignments somewhat uncertain. With excitation at 300 nm, band positions were: 0–0 band, 418 nm in ethanol, 412 nm in isopentane; λ_{max}, 443 nm in ethanol, 450 nm in isopentane. The mean radiative lifetime was 156 msec (ethanol glass). Authenticity of the phosphorescence spectra was indicated by comparison of the excitation and absorption spectra. Additionally, capillary glpc analysis indicated purity of samples at ≥99.9%.

Sensitized Irradiation of 3-Ethylidene-2,2,5,5-tetramethylcyclohexanone at 77°K in Isopentane. To 0.50 ml of Spectrograde iso-pentane in a Pyrex 5-mm nmr tube was added 50.0 mg (0.278 mmol) of the ethylidene ketone as a 15% E:85% Z isomer mixture and 15.0 mg (0.076 mmol) of xanthone (Aldrich, recrystallized twice from ethanol). The solution was immersed in a Pyrex dewar at 77°K and irradiated with an external 450-W mercury lamp. After 5 hr, no visible change could be detected by 100-MHz nmr spectroscopy. When irradiation was continued under identical conditions except at room temperature, only 4 hr irradiation produced a 30% E:70% Z mixture of isomers, as analyzed by nmr.

The Continuous Diradical as Transition State.   Internal Rotational Preference in the Thermal Enantiomerization and Diastereoisomerization of *cis*- and *trans*-1-Cyano-2-isopropenylcyclopropane

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Abstract: Of the three most rapid rearrangements undergone by the disubstituted cyclopropanes of the title, the two geometrical isomerizations cannot be concerted in the usual sense of continuous overlap of orbitals and are thus able to reveal differences among the internal rotations requisite to the rearrangement. The three rearrangements are independent of each other, proceed at their maximum rates at the beginning of the reaction, and can be accommodated only inadequately (32%) by a conventional diradical intermediate within which only one internal rotation at a time is permitted. In our estimation this is the first example of the opening of a three-membered ring which has been so labeled by substituents and optical activity as to reveal the need for a change in mechanistic hypothesis. In the dynamic aspects of bond breaking we believe to have found the basis for a consistent conceptual scheme, that of the continuous diradical as the internally rotationally coupled extension of stretching vibrational modes. Incapable of being trapped, the continuous diradical represents families of energetically and orbitally not concerted transition states the stereochemical differences among which originate in energetic preferences among the observationally independent, internally rotational components.

Singlet trimethylene was put forward many years ago to rationalize the constitutional isomerization of cyclopropane to propylene.[1] This simple mechanistic hypothesis has had the undeniable merit of compatibility with the subsequently discovered cis–trans geometrical isomerization[2] and racemization of optically active cyclopropanes,[3,4] as well as with the varied rearrangements of cyclopropanes substituted by one[5] or two vinyl groups,[6] by a carbonyl function, or by a combination of carbonyl and vinyl groups.[7,8]

Recent years have seen major attention directed toward a more precise definition of the nature and role of trimethylene.[9,10] Is it an intermediate of sufficiently long life to be trapped in a second-order or pseudo-

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first-order reaction or to suffer the internal rotations structurally necessary to accommodate the numerous configurational rearrangements? Is it being confused with the transition state of a concerted rearrangement involving significant continual bonding between the two radical ends? Since different answers may be expected from cyclopropanes of different types of substitution, queries about the radical may need repeated asking. Although an independent, intermediary role for the singlet diradical has received little encouragement from theory, its exclusion must be tentative in view of the doubtful reliability of the quantitative results of theory as it is presently applicable to organic reactions.

In this paper we present observations of a new type which warrant redefinition of the role of the diradical as a vibrational manifold of states. Its compressional boundaries combine the structures of starting material and product. As a transition state it may be any one of a number of vibrational modes of the assembly of atoms and not the customary transition state through which the transformation of a normal vibrational mode into a translational degree of freedom is accomplished. The design and execution of experiments intended to permit recognition of the need for redefinition have been slow. With the present work we believe the weight of evidence has become sufficient to justify the outline of a new conceptual scheme, although our earlier contributions have appeared to point in the same direction. For those less interested in organic chemical details, reading of the next section may be deferred.

Methyl 2-Isopropenylcyclopropane-1-carboxylates: (—)-trans-II and (—)-cis-II

The original purpose of this work was the elucidation of the configurational characteristics of the rearrangement of vinylcyclopropane to cyclopentene[2h,11] with special attention to the question of the admissibility of concertedness in general and later more specifically in terms of the Woodward–Hoffmann generalizations.[12] Through the use of the carboxylate group to introduce chirality and provide convenience of resolution and through the use of the isopropenyl group to ensure chirality in the product, a system was designed which made it possible to explore the preservation of optical activity during the rearrangement. Shortly after the work began, it became clear that racemization and a cis-trans interconversion were the more rapid reorganizations and that some optical activity was preserved in the latter rearrangement. This observation entirely parallels the original discovery of Willcott and Cargle on 2-deuteriovinylcyclopropane that geometrical isomerization is faster than rearrangement to cyclopentene.[2g] The retention of some measure of optical activity stands in conflict with what might have been "predicted by a free rotating diradical intermediate," the conclusion reached by Willcott and Cargle on the basis of their study of the kinetics of rearrangement of cis-2,-3-dideuteriovinylcyclopropane.[2h]

The starting material, trans-cyclopropane-1,2-dicarboxylic acid (trans-I), can be prepared conveniently by a modification of McCoy's method.[13] Under his con-
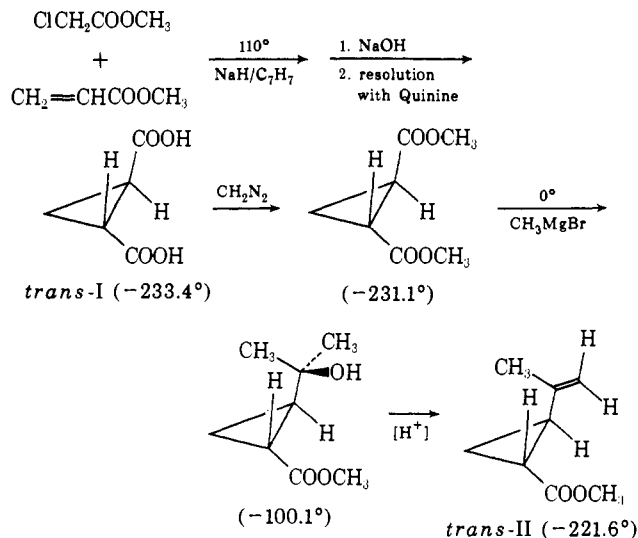

Figure 1. Preparation of materials. Specific rotations at 578 nm in absolute ethanol.

ditions, methyl acrylate and ethyl chloroacetate give a mixture of predominantly cis-cyclopropane-1,2-dicarboxylate in 34–45% of theory. Under conditions which also serve to establish equilibrium between the cis isomer and its thermodynamically more stable trans relative,[14] essentially pure trans can be obtained. Thus, sodium methoxide in dimethyl sulfoxide at 30–40° not only catalyzes the condensation but effects equilibration to the trans isomer (40–50% of theory). Sodium hydride in toluene, the preferred reagent below 100°, affords a mixture in 60% of theory consisting of the cis isomer (60%) and the trans isomer (40%), while at 110–115° it affords the trans isomer in 65% of theory, free of a by-product obtained with DMSO–sodium methoxide.

An incomplete resolution using brucine, reported by Buchner and von der Heide,[15] is convenient for the preparation of essentially pure (+)-trans-I. Either 1 or 2 equiv of quinine conveniently affords (—)-trans-I, $[\alpha]_{578}$ —231°, and its (+) enantiomer. A specific rotation, $[\alpha]_D$ 228°, is reported for a sample obtained by oxidation of trans-2-phenylcyclopropane-1-carboxylic acid.[16] The absolute configuration of (—)-trans-I, although not essential to the present work, is known through its relationship to trans-1,2-dimethylcyclopropane[16] and, through the latter, to active amyl alcohol.[17] Active dimethyl ester of presumably undiminished optical purity is obtained by treatment of (—)-trans-I with diazomethane. This ester can be converted to (—)-(trans-2-carbomethoxycyclopropyl)dimethylcarbinol in excellent yield by treatment with slightly more than the required amount of methylmagnesium bromide at 0°. Dehydration to the desired product, methyl (—)-trans-2-isopropenylcyclopropane-1-carboxylate, [(—)-trans-II], proceeds smoothly in the presence of a trace of acid (see Figure 1) in a reaction similar to that of Volkenburgh, Greenlee, Derfer and Boord.[18]

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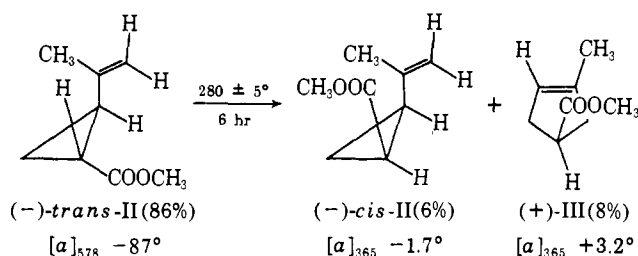(16) Y. Inouye, T. Sugita, and H. M. Walborsky, Tetrahedron, 20, 1695 (1964).
(17) W. von E. Doering and W. Kirmse, Tetrahedron, 11, 272 (1960).
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Figure 2. Results of an incomplete thermal reorganization of (−)-*trans*-II to (−)-*cis*-II and (+)-III during which *trans*-II was 59% racemized.

Thermal Rearrangements of (−)-*trans*-II and (−)-*cis*-II

Thermal rearrangements of (−)-*trans*-II, conducted between 275 and 285° in Pyrex ampoules in the presence of diphenylamine, led to methyl *cis*-2-isopropenyl-cyclopropane-1-carboxylate (*cis*-II) and methyl 1-methyl-1-cyclopentene-4-carboxylate (III). After being heated 23 hr at 277 ± 3°, (−)-*trans*-II, 66% of which was recovered with 5% of its original activity remaining, yielded *cis*-II and III in 5 and 29% of the theoretical amount, respectively. The results of rearrangement at 280 ± 5° for 6 hr are outlined in Figure 2. In both the longer and shorter experiment the ratio of recovered *trans*-II to *cis*-II was 14.0. If this steady-state ratio corresponds approximately to the equilibrium ratio, the free energy difference is 2.90 kcal/mol.

With respect to the slower rate of the rearrangement of vinylcyclopropane to the cyclopentene (III), the allylic-like radical must have the methyl group and the hydrogen atom cis to each other in order for this rearrangement to occur.[19] In contrast, the more rapid reaction, the geometrical isomerization of *trans*-II to *cis*-II, may take place with the allylic radical in either configuration.

Authentic methyl 1-methylcyclopentene-4-carboxylate was synthesized from diethyl 3-methyl-3-cyclopentenedicarboxylate.[20] The configurational characteristics of this rearrangement have been determined subsequently in the related example of 1-methyl-4-cyanocyclopentene.[21]

Methyl *cis*-2-isopropenylcyclopropane-1-carboxylate (*cis*-II) has been synthesized to help confirm the structure of the rearrangement product and has been resolved in order to permit examination of the fate of optical activity on heating. The reaction of isoprene with photolytically generated carbethoxycarbene[22] leads to four products, two of which are easily recognized from their nmr spectra as ethyl 2-methyl-2-vinylcyclopropane-1-carboxylate, one of which is identical with *trans*-II (ethyl ester), and the last of which is identical with the supposedly *cis*-II (ethyl ester) and is assigned that structure by exclusion. *cis*-II was obtained in optically active form by resolution of its carboxylic acid with ephedrine.

When (−)-*cis*-II was heated for 4 hr at 280 ± 10°, it was recovered, about 98% racemized, in 6% of theory, *trans*-II was obtained in 76% of theory with laevorotatory enantiomer in slight excess (1.5%), and methyl

1-methylcyclopentene-4-carboxylate (III) was isolated in 18% of theory with the dextrorotatory enantiomer favored to the extent of approximately 4%.[21]

Focus on Enantiomerization and Diastereoisomerization. Shift to Nitrile

The striking feature of this first experiment is the retention of some optical activity both in the geometrical isomerization and in the rearrangement to the cyclopentene (see Figure 2). It can therefore be concluded of both processes that a freely rotating diradical, which would lead to complete racemization, cannot be the exclusive intermediate.

Conventional concertedness cannot be considered for a process which passes through a zero-bonding stage having an orthogonal relationship between two sets of π orbitals. The conclusion seems as valid within the framework of Woodward–Hoffmann frontier orbital theory[23] as within the Berson–Salem[24] addendum of energy lowering through subjacent orbitals. Although the degree of conformational selectivity remains to be determined, at least of the formation of *cis*-II from *trans*-II, it is concluded that factors other than the symmetry of orbitals must be operating.

That some optical activity is retained in this particular instance is the more remarkable since each half of the diradical is stabilized by three-atom delocalization, the isopropenyl portion by 12–13 kcal/mol[25] and the carbomethoxy portion by ∼8 kcal/mol.[26] A routine calculation based on the assumption of log A = 13–15 and first-order kinetics converts the 41% of optical activity remaining in (−)-*trans*-II after 6 hr at 280° (k = 4 × 10^{-5} sec^{-1}) into an activation energy of 44–49 kcal/mol. These values are 15–20 kcal/mol lower than that for the geometrical isomerization of unsubstituted cyclopropane.[2a] Consequently, collapse of the diradical to products might have been expected to be slower than internal rotation in this instance. But of this expectation, it is conceded that the factors which might govern the response of the relative rates of internal rotations to changes in structure have not been elucidated and that a recent reexamination indicates that the allylic radical combines with simple radicals at undiminished rate.[27] Regardless, it is clear that internal rotation of the carbomethoxy group and the isopropenyl group at identical rates would have led to racemic *cis*-II.

Of the two lines of mechanistic inquiry opened in the initial phases of this investigation, that concerned with the elucidation of the configurational characteristics of the degenerate cyclopropane rearrangement was selected for immediate further investigation over that involving the vinylcyclopropane rearrangement. No matter how the configurational properties of the latter rearrangement might be dissected, the outcome would be rationalizable as the consequence of either the ($_\sigma2_s$ + $_{\pi'}2_a$) or the ($_\sigma2_a$ + $_{\pi''}2_s$) processes allowed by the frontier orbital theory of Woodward and Hoffmann[23] or

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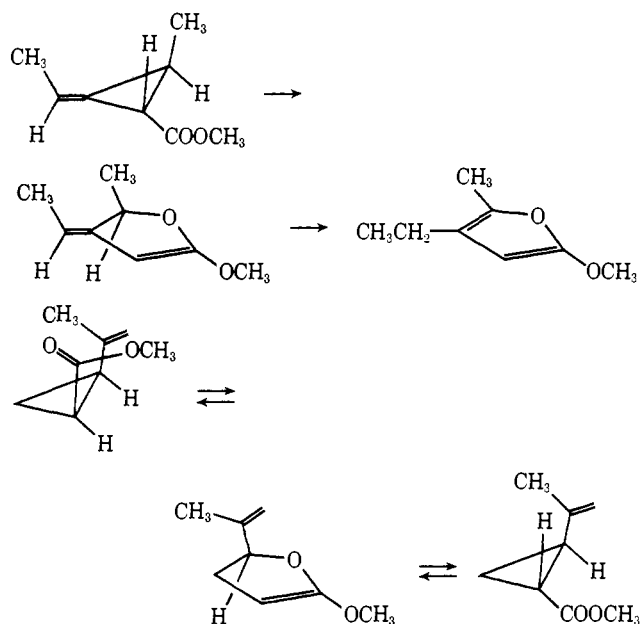
(27) J. J. Throssell, *Int. J. Chem. Kinet.*, 4, 273 (1972).

Figure 3. Real and hypothetical involvement of carbonyl group in thermal reorganization of methylenecyclopropane and vinylcyclopropane, respectively.
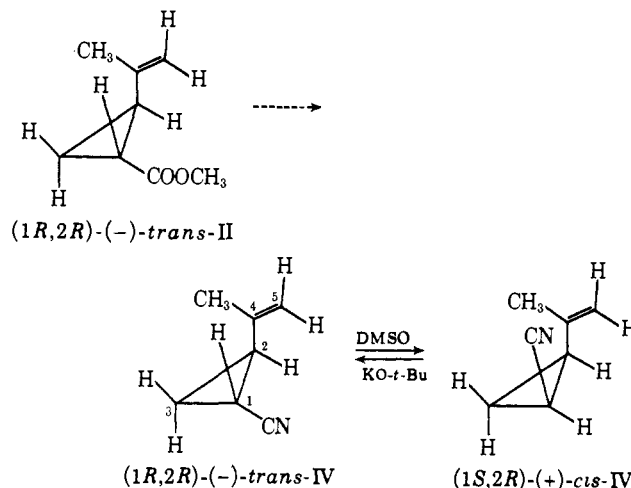
(1R,2R)-(−)-trans-II

(1R,2R)-(−)-trans-IV   (1S,2R)-(+)-cis-IV

DMSO
KO-t-Bu

Figure 4. Preparation and configurational interrelationship of trans-1-cyano-2-isopropenylcyclopropane.

its equivalent, the Möbius, aromatic formulation of Dewar–Heilbronner–Zimmerman.[28] Should there be balking at the steric implausibility of the $({}_\sigma 2_s + {}_{\pi''}2_a)$ process, the subjacent orbital hypothesis of Berson and Salem $({}_\sigma 2_s + {}_{\pi''}2_s)$ would inevitably suggest itself as an alternative. By contrast, the diastereomeric interconversion of the cis and trans isomers, which is not easily imagined to proceed over continuously bonding configurations, can be assumed to be nonconcerted and the more directly to be related to the role and nature of trimethylene and "ring opening."

Further penetration requires determination of the relative rates of formation of dextro- and laevorotatory enantiomeric products without the disturbing attenuation of racemization in the starting diastereomer. It also requires establishment of the relative configurational relationship of cis- and trans-II in order to give structural expression to the configurational preferences. The successful resolution of these requirements would allow the question to be answered whether enantiomerization (or racemization) and diastereoisomerization are independent or consecutive processes.

At about this time in the present investigation, Dr. Ludmila Birladeanu discovered a disturbing interference by an ester group during the thermal rearrangement of a methylenecyclopropane, in which the oxygen atom of the carbonyl group became permanently set in a covalent bond.[29] If permanent involvement of an ester oxygen occurs in even one instance, then its covert, fleeting involvement becomes a source of insistent worry in all instances. In the present rearrangement, the intervention of such an interaction, particularly if it were transient, reversible, and not easily to be detected, would detract from, if not destroy, the validity of any inferences about the hypothetical diradical (see Figure 3).

This pitfall can be avoided by replacing the ester group with the nitrile group. The convenience of the carboxylic acid in resolutions is retained, albeit at the bearable expense of the extra steps involved in the conversion of a carboxylic acid group to nitrile. The linearity of the nitrile presents an unfavorable angular disposition for a cyclic interaction of the type hypothesized for the ester. Such an interaction would require the highly strained combination of allenic geometry and a five-membered ring. The nitrile offers a kinetically facile, base-catalyzed epimerization and a thermodynamically significantly smaller steric bulk[30] to help with the establishment of configurational interrelationships. The nitrile also offers the possibility of confirmation of structure by analysis of the lanthanide-induced shifts in the nuclear magnetic resonance spectrum according to the method of Willcott and Davis.[31] Finally, the nitrile group should lower the activation energy for bond breaking in the thermal reorganizations.[32] Preliminary experiments suggest that the energy-lowering propensity may actually exceed that of the ester group.[21] (Here also the organic chemically disinclined reader may proceed to the next section.)

The starting point for optically active nitrile is (−)-trans-II (see Figure 4) which can be treated with ammonia to give the corresponding amide, (−)-trans-2-isopropenylcyclopropane-1-carboxamide, in one step. A higher overall yield results from the three-step sequence involving saponification to the acid, conversion of its triethylamine salt to the mixed anhydride with ethyl chloroformate, and saturation with ammonia gas. Conversion of the amide to the nitrile is conveniently effected in high yield through the reaction of pyridine and p-toluenesulfonyl chloride. The optical purity of the resulting (−)-trans-1-cyano-2-isopropenylcyclopropane [(−)-trans-IV] has not been determined, but there is little reason to suspect racemization during any of the

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steps in the preparation. Its specific rotation, $[\alpha]\text{D}$ $-203.4°$, is high enough to permit measurements with satisfactory accuracy. Although absolute configurations are irrelevant to this investigation, the $1R,2R$ configuration seems assured for $(-)$-trans-IV through its derivation from $(1R,2R)$-$(-)$-cyclopropane-1,2-dicarboxylic acid [$(-)$-trans-I] (vide supra).[16,17]

The diastereomeric $(+)$-cis-IV is conveniently obtained by treatment of $(-)$-trans-IV with potassium tert-butylate in dimethyl sulfoxide at 15°.[33] At equilibrium, which is reached within 1 min and can be achieved in either direction, the ratio of trans- to cis-IV is 64.2:35.8 which corresponds to $K = 1.79 \pm 0.15$ and $\Delta G = -334$ cal/mol. Steric interaction of the cyano group is thus much smaller than that of the ester group $(-2900$ cal/mol).[14] Isolation and purification of the cis isomer by gas chromatography is tedious and requires care but is capable of providing material completely free of the trans isomer. Since this procedure almost certainly involves epimerization of the cyano group by removal of the hydrogen atom α to the cyano group and not by removal of the much more weakly acidic hydrogen α to the isopropenyl group, the configurational relationship of $(+)$-cis- and $(-)$-trans-IV seems assured. Under the conditions of epimerization, there is no racemization within experimental error.

The constitution and the configurations of $(-)$-trans-IV and $(+)$-cis-IV are confirmed by examination of their nmr spectra. The chemical shifts of individual hydrogen atoms can be estimated from lanthanide-shifted spectra[31] by extrapolation to zero concentration of the lanthanide agent. These chemical shifts are reported as average values in Table I. From the fine

Table I. Shifts in Proton Magnetic Spectra of trans-IV and cis-IV Induced by Europium, Praseodymium, and Ytterbium Expressed Relative to the Hydrogen at C_3 trans to the Cyano Group as 1.00

H-type[a]	Eu(fod)₃	Pr(fod)₃	Yb(dpm)₃	Ppm (δ)
trans-IV				
1-H[b,c]	2.426	2.167	1.844	1.29
2-H (cis)[b-d]	1.509	1.574	1.515	2.02
3-H (cis)[b,c,e]	1.458	1.491	1.508	1.28
3-H (trans)[b,d,e]	1.000	1.000	1.000	1.15
4-CH₃	0.473	0.516	0.548	1.70
5-H (Z)	0.520	0.562	0.543	4.79
5-H (E)	0.353	0.357	0.402	4.81

H-type[a]	Yb(fod)₃	Ppm (δ)
cis-IV		
1-H	1.968	1.21
2-H (trans)	1.045	1.78
3-H (cis)	1.585	1.05
3-H (trans)	1.000	1.09
4-CH₃	0.923	1.87
5-H (Z)	0.561	4.99
5-H (E)	0.989	4.84

[a] Numbering system as in Figure 4; cis and trans refer to the cyano group. [b] $J_{cis:1,3} = J_{cis:2,3} = 9$ Hz. [c] $J_{trans:1,3} = J_{trans:1,2} = 5$ Hz. [d] $J_{trans:2,?} = 6.5$ Hz. [e] $J_{gem:?,3} = 5$ Hz.

structure of the resonance separated by europium, the most acceptable of the three lanthanides in respect of line broadening, multiplicities and approximate cou-

(33) H. M. Walborsky and F. M. Hornyak, J. Amer. Chem. Soc., 77, 6026 (1955); R. G. Bergman, ibid., 91, 7405 (1969).

pling constants can be extracted. Of particular value in this structural assignment are the relative responses of the different types of hydrogen to varying concentrations of lanthanide shift reagents. Since recent work has given strong support to the contention that the complexed system, carbon–carbon–nitrogen–lanthanide, is linear, the relative responses can be considered a direct measure of the function, $(3 \cos^2 \theta - 1)/r^3$, which describes the pseudocontact shift, provided the contact shift is negligible. Primarily by examination of the shift of 2-H and secondarily from the protons of the isopropenyl groups, the assignment of the cis and trans configurations seems assured. All attempts to extract the conformation of the isomers from the relative rates of shift of the protons in the isopropenyl [4-CH₃, 5-H (Z), and 5-H (E)] group have failed. Although a plot of the statistical R factor against angle of rotation can be computed and indeed reveals two minima at intuitively reasonable angles, as soon as the more likely model of two (or more) conformations in equilibrium is considered, no conclusion of any sort can be drawn. In fact in this case, and we believe generally, combinations of conformations which are unacceptable when taken singly, produce solutions of insidiously attractive, low R values.

The Three Independent Processes: Enantiomerization and Diastereoisomerization

Incomplete thermal rearrangements of trans-IV at 228° for 130 and 260 min in the gas phase leads to cis-IV in 11.8 and 18% of theory, respectively, and to 1-methyl-4-cyanocyclopentene (V) in 0.9 and 1.9% of theory, respectively. The cyclopentene, V, is strongly favored thermodynamically and becomes the major product on long heating at higher temperature. Thus, V is the only product after 19 hr at 272° in benzene solution or 78% after 18 hr at 262° in the gas phase (along with 5% of cis-IV and 17% of trans-IV).

The kinetics of the thermal diastereoisomerization of racemic trans-IV and cis-IV at the boiling point of naphthalene (217.8°) is examined in both directions. The experimental data are given in Tables II and III.

In handling the data, the much slower, irreversible formation of V is neglected. This approximation is justified by the fact that cis-IV and trans-IV are interconverted about ten times faster than either is converted to V. Rate constants can then be calculated from the usual expression for reversible first-order reactions, $-\log [(AK - B)/(A_0K - B_0)] = t(k_{t,c} + k_{c,t})/\ln 10$, where A and B are the % of trans and cis, respectively, and $K = k_{t,c}/k_{c,t}$. The data in Tables II and III for geometric isomerization are plotted in Figure 5. The values of the slope $(k_{t,c} + k_{c,t})/\ln 10$ determined by the least-squares treatment of the data from three different runs along with the values of equilibrium constant (calculated by trial and error) and the individual rate constants are reported in Table IV.

On the highly questionable assumption that the value of the equilibrium constant at 15° in dimethyl sulfoxide $(-334$ cal/mol; $K = 1.79 \pm 0.06)$ can be combined with the value in the gas phase at 217.8° $(-983$ cal/mol; $K = 2.74)$, thermodynamic parameters for the reaction, cis-IV $\rightleftharpoons$ trans-IV, can be computed: $\Delta H = +588$ cal/mol and $\Delta S = 3.20$ cal/deg. If substantiated by proper experiments this result suggests a smaller steric factor

Table II. Thermal Racemization and Diastereoisomerization of (−)-trans-IV^a in Gas Phase at 217.8°

| Time, min | Recovered (−)-trans-IV^b | | | | | Product cis-IV^b | | | | |
	[α]^{27}D, deg	[α]$^{27}_{365}$, deg	Concn^b	Opt purity,^{c} %	Con-version,^{d} %	[α]^{27}D,^{e} deg	[α]$^{27}_{365}$,^{e} deg	Concn^b	Opt purity,^{c} %	Re-covery,^{f} %
46.5	−195.4	−668.0	0.4643	96.36	2.53*	−71.3	−242.5	0.1963	35.25	99.70
	−196.6	−670.0	0.4298			−72.1	−237.9	0.3547		
90.0	−188.0	−641.6	0.4718	92.38	4.72	−70.2	−239.1	0.3705	34.19	99.80
	−187.8	−641.5	0.4868			−68.8	−235.7	0.1222		
150.0	−178.3	−609.7	0.4963	87.63	7.42	−66.4	−227.6	0.5421	32.20	99.80
	−178.2	−609.1	0.4523			−64.6	−226.6	0.3871		
220.0	−165.8	−564.8	0.4548	81.36	10.17	−63.3	−216.4	0.4596	30.55	99.40
	−165.2	−563.5	0.4504			−61.0	−210.5	0.2855		
310.0	−151.9	−516.7	0.5068	74.48	13.05	−57.7	−197.6	0.3238	28.36	99.50
	−151.1	−514.0	0.4619							

^{a} Starting material of [α]^{27}D −203.4°, [α]$^{27}_{365}$ −692.2° (c 0.4888, cyclohexane). ^{b} g/100 ml, all specific rotations are determined twice in Spectrograde cyclohexane. ^{c} Calculated from the average value of the two measurements of specific rotations at 589 nm at each time interval. ^{d} Determined by glpc analysis of the product mixture using Digital Integrator. These values (±0.02) were obtained on racemic trans-IV and are the means of two glpc analyses at each point, *46.0 min point. Conversion is ratio of cis-IV to the sum of cis- and trans-IV times 100. The starting material contained trans-IV and cis-IV in the ratio 99.48:0.52, respectively, and the reported % conversions have been corrected. ^{e} Specific rotation of trans-IV obtained by epimerization of the product cis-IV. ^{f} Total recovery of cis- and trans-IV based on benzonitrile as an internal standard.

Table III. Thermal Racemization and Diastereoisomerization of (+)-cis-IV^a in Gas Phase at 217.8°

| Time, min | Recovered cis-IV^b | | | | | Product trans-IV | | | | |
	[α]^{27}D, deg	[α]$^{27}_{365}$, deg	Concn^c	Opt purity, %	Con-version,^{d} %	[α]^{27}D, deg	[α]$^{27}_{365}$, deg	Concn^c	Opt purity, %	Re-covery,^{e} %
46.0	−171.3	−587.6	0.2347	95.59	6.91	−63.5	−214.3	0.1717	35.43	99.50
91.5	−161.2	−549.0	0.2705	89.95	13.28*	−60.8	−208.9	0.1925	33.92	99.85
150.0	−151.5	−519.5	0.3744	84.54	20.55	−57.8	−198.5	0.1627	32.25	99.81
220.0	−136.1	−465.4	0.3427	75.95	28.53	−53.7	−183.3	0.1675	29.97	99.65
310.0^f					36.50					99.40

^{a} Starting material of [α]^{27}D +3.9°; specific rotation of the corresponding trans-IV (obtained by epimerization): [α]^{27}D −179.2°, [α]$^{27}_{365}$ −617.1° (c 0.274, cyclohexane). ^{b} Specific rotation of samples of trans-IV obtained by epimerization of the recovered cis-IV at each time interval. ^{c} g/100 ml in Spectrograde cyclohexane. ^{d} Determined by glpc analysis of the product mixtures using Digital Integrator. These values (±0.02) were obtained on racemic cis-IV and are the means of two glpc analyses at each point, *90.0 min point. Conversion is ratio of trans-IV to the sum of cis- and trans-IV times 100. ^{e} Based on benzonitrile as an internal standard. ^{f} Optical activity was not determined at this point.

for the nitrile group than for the hydrogen atom and a compensating entropy factor possibly associated with a greater torsional freedom in the trans isomer.

With optically active cis-IV and optically active trans-IV available, the rate of racemization of starting nitrile and the degree of retention of optical activity in the diastereoisomeric product can be determined. In view of the reversibility of the diastereoisomerization, care is required to determine that the decrease in optical activity of starting nitrile is a direct, independent reaction and not the consequence of rearrangement of already optically degraded diastereoisomeric product back to starting nitrile. Reliable distinction between these alternative pathways of racemization is best accomplished by extrapolation to zero time of a set of observations themselves made as near to zero time as experimentally feasible. The same requirement applies to the determination of the distribution of enantiomers in the diastereoisomeric nitrile. To be as free of disturbance as possible by reverse rearrangement, optical activity should be determined as near the beginning of the reaction as possible. The condition is more difficult to satisfy in the rearrangement of trans-IV to thermodynamically less favored cis-IV, since the latter racemizes and rearranges back to trans-IV faster than trans-IV racemizes and rearranges back to cis-IV. Experimental difficulties with cis-IV are aggravated further by the woefully low value of its specific rotation
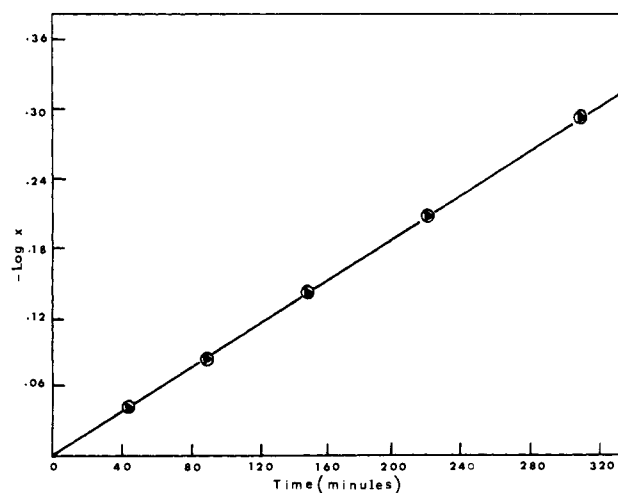
Figure 5. Plot of −log x [x = (AK − B)/(A$_0$K − B$_0$)] vs. t at 217.8° of the data in Tables II and III, equilibrium constant, K = 0.3648 = [cis]/[trans]: geometric isomerization (diastereoisomerization) of trans-IV (○) and cis-IV (▲).

([α]^{27}D +4.4°; [α]$^{27}_{365}$ −49.7° from trans-IV, [α]^{27}D −203.4°). A procedure has been developed in which, first, pure cis-IV is isolated by careful gas chromatography and, second, is converted by base-catalyzed equilibration to a mixture of cis- and trans-IV, from which trans-IV is isolated in pure form and on which the

Table IV. First-Order Rate Constants for Geometric Isomerization of *trans*-IV and *cis*-IV

Run no.	$10^6(k_{t,c} + k_{c,t})$,[c] sec^{-1}	$K^f = k_{t,c}/k_{c,t}$	$10^6 k_{t,c}$, sec^{-1}	$10^6 k_{c,t}$, sec^{-1}
1[a]	37.34 ± 0.10[d]	0.3648	9.98 ± 0.03[g]	27.36 ± 0.07[g]
	37.33 ± 0.26[e]			
2[b]	35.73 ± 0.30[d]	0.3640	9.54 ± 0.08	26.20 ± 0.21
	35.74 ± 0.28[e]			
3[b]	38.19 ± 1.96[d]	0.3570	10.04 ± 0.41	28.14 ± 1.16
	38.17 ± 1.18[e]			

[a] Data are given in Tables II and III. [b] Data are given in Table VII. [c] Obtained by the least-squares treatment of the data. [d] Starting from *trans*-IV. [e] Starting from *cis*-IV. [f] Using a least-squares computer program for minimization, the value of K was found by trial and error to give identical values of the slope of the line, $-\log [(AK - B)/(A_0K - B_0)] = t(k_{t,c} + k_{c,t})/\ln 10$ starting from *trans*-IV and *cis*-IV. [g] Subsequent to these calculations in neglect of the formation of cyclopentene, the results were recalculated by an iterative process including all four rate constants. A best fit is obtained when $k_{t,c} = 10.10$ and $k_{c,t} = 27.03 \times 10^{-6}$ sec^{-1}. Details will be published later.[21]
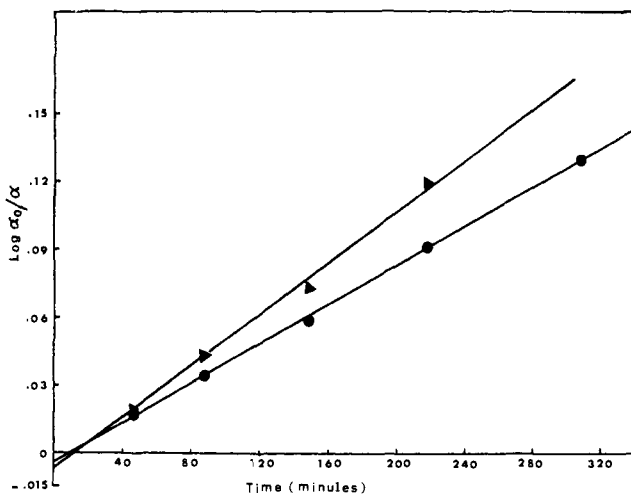

Figure 6. Plot of decrease in optical activity (log α_0/α) with time at 217.8°, the data being taken from Tables II and III: racemization of (−)-*trans*-IV (●) and racemization of (+)-*cis*-IV (▲). The heavy lines are calculated by the method of least squares.

measurement of optical activity is made. In control experiments it has been established that optically active *trans*-IV is not racemized during the equilibration procedure.

Racemization of (−)-*trans*-IV (that is, loss of optical activity in recovered (−)-*trans*-IV) follows pseudo-first-order kinetics over the first 25% of the reaction. As can be seen from Figure 6, there is no discernible intimation of the S shape which would characterize the racemization if this process were to depend on the back rearrangement of initially formed *cis*-IV. Also from Figure 6 it appears that a straight line is a reasonable representation of the data over this early part of the reaction and its slope approximates the slope at zero time. The specific rate constant for loss of optical activity in recovered (−)-*trans*-IV (T), $(k_\alpha)_T$, is determined by the method of least squares from the five points ranging from 3.63 to 25.5% of racemization given in Table II and has the value

$$(k_\alpha)_T = (16.3 \pm 0.20) \times 10^{-6} \text{ sec}^{-1} \text{ at } 217.8°$$

The racemization of (+)-*cis*-IV (C) also follows pseudo-first-order kinetics (see Figure 6) and shows no sign of an S shape. From the data in Table III, the specific rate constant for loss of optical activity in recovered (+)-*cis*-IV (C) may be determined by the method of least squares and has the value

$$(k_\alpha)_C = (21.7 \pm 1.1) \times 10^{-6} \text{ sec}^{-1} \text{ at } 217.8°$$

An attempt to correct these values for back reaction can be made by assuming that half the amount of product for any given point was available for reconversion to starting material of $(0.35)^2$ optical purity. Least-squares treatment of such corrected data including the origin gives $(k_\alpha)_T = 14.7 \pm 0.2$ and $(k_\alpha)_C = 19.4 \pm 0.8 \times 10^{-6}$ sec^{-1}, but in the following discussion the uncorrected values are used.

Both *trans*-IV and *cis*-IV lose optical activity by a primary process which is independent of the prior formation of diastereoisomer. Although later on in the reaction, racemization must increasingly arise through the intervention of the diastereomer (*e.g.*, (−)-*trans*-IV → (+)-*cis*-IV → (+)-*trans*-IV), at the beginning of the reaction the process is direct, (−)-*trans*-IV → (+)-*trans*-IV and (+)-*cis*-IV → (−)-*cis*-IV, without the intermediate intervention of the epimeric diastereoisomer. In the ensuing discussion, loss of optical activity shall be treated in terms of rates of enantiomerization, k_{TT} and k_{CC} (see Figure 8).

$$k_{TT} = (k_\alpha)_T/2 = 8.2 \times 10^{-6} \text{ sec}^{-1}$$

$$k_{CC} = (k_\alpha)_C/2 = 10.8 \times 10^{-6} \text{ sec}^{-1}$$

Diastereoisomerization of both (−)-*trans*-IV and (+)-*cis*-IV leads to a mixture of enantiomers, the ratios between which have been evaluated at zero time. The degree of optical activity in *cis*-IV produced by diastereoisomerization of (−)-*trans*-IV (and that in *trans*-IV from (+)-*cis*-IV) declines in linear fashion over the 25% of reaction taken under observation (see Figure 7). Owing to increasing racemization in the starting material and the diastereoisomeric product, the degree of optical activity is not followed beyond this point nor would it be helpful in determining the maximum degree of optical activity in diastereoisomeric product. Least-squares treatment of the relevant data in Tables II and III gave the intercepts at zero time, from which it is calculated that the rearrangement of (+)-(1S,2R)-*cis*-IV (C) generates *trans*-IV consisting 68.4% of (−)-(1R,2R) (T) and 31.6% of (+)-(1S,2S) (T) configuration while rearrangement of (−)-(1R,2R)-*trans*-IV (T) leads to 68.2% (+)-(1S,2R) (C) and 31.8% of (−)-(1R,2S)-*cis*-IV (C) (see Figure 8).

Both diastereoisomers rearrange as if rotation of the nitrile group were easier than rotation of the isopropenyl group. Thus, the ratio of (C) (rotation of the nitrile) to (C) (rotation of isopropenyl) produced from (T) is 2.15, while the comparable experimental ratio of (T) (rotation of nitrile) and (T) (rotation of isopropenyl) produced from (C) is 2.17 ($\Delta\Delta G = 750$ cal/mol).
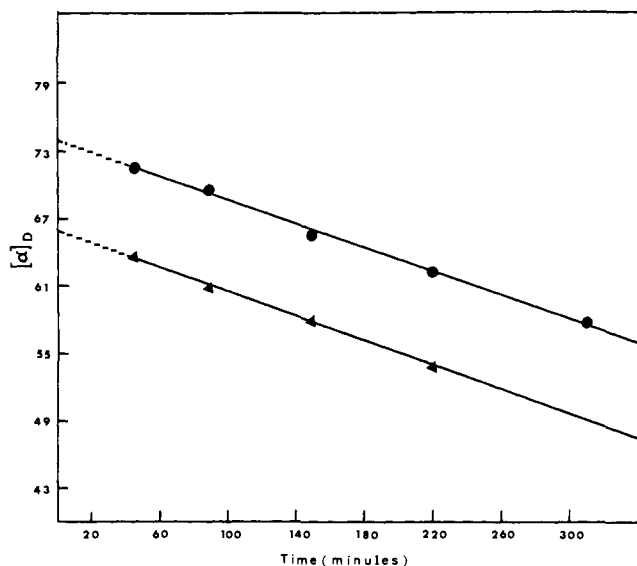
Figure 7. The plot of specific rotations of diastereoisomeric product against time: of cis-IV from (—)-trans-IV (●) and trans-IV from (+)-cis-IV (▲); the data were taken from Tables II and III, respectively. Note that, if the optical purity of starting (—)-trans-IV is assumed to be 100%, that of (+)-cis-IV is 88%.

Preferential Rotational Propensities

Three mutually independent, degenerate thermal rearrangements of cyclopropane have thus been revealed. Each has its maximum rate at the beginning of the reaction and none is the consequence of another. The three processes are enantiomerization and diastereoisomerization to a pair of optical antipodes. This specific example of 1-cyano-2-isopropenylcyclopropane illustrates a general procedure for bringing internal rotational preferences to light.

In the general system, the four rate constants (k_{TC}, k_{TC}, k_{CT}, and k_{CT} of Figure 8) associated with diastereoisomerization can be factored by the equilibrium constant (K) and by the preference (R_A) of A to rotate over B. It is a property of the system that R_A must be a thermodynamically rigorous constant independent of whether it is measured from optically active cis or trans. This conclusion follows from the definition of K [(7) of

$$k_{CT} = k_{TC}K \text{ and } k_{CT} = k_{TC}K \quad (11)$$

Figure 8] and the definition of R_A [(8) of Figure 8], whence

$$k_{TC}R_A/k_{TC} = 1 \quad (12)$$

Since

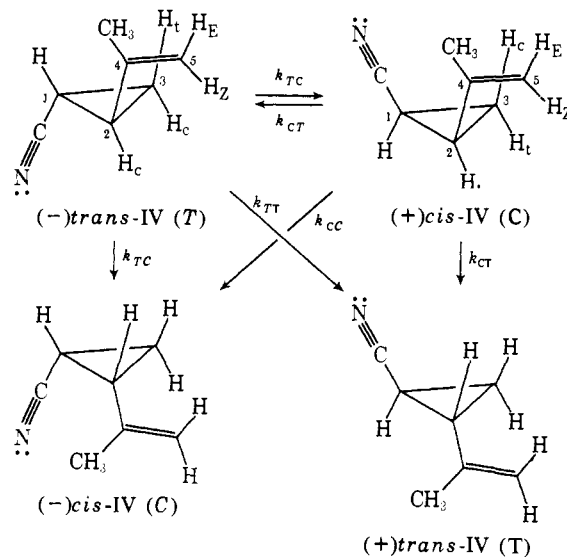$$\frac{k_{CT}}{k_{TC}} = \left(\frac{k_{CT}}{k_{TC}}\right)\frac{R_A}{R_A}$$

$$\frac{k_{CT}R_A}{k_{CT}} = \frac{k_{TC}R_A}{k_{TC}} = 1 \quad (13)$$

it follows that the ratio of rates of rearrangement from (+)-cis is also a thermodynamically precise measure of R_A since

$$k_{CT}R_A = k_{CT} \text{ or } R_A = k_{CT}/k_{CT} \quad (14)$$

and that the rate constants may be factored in terms of k_{TC}, R_A, and K [(1), (2), (4), and (5) of Figure 8].

In practice the system can be determined by as few as

Experimental Results [temp = 217.8° (490.96° K)]

$k_{TC} = 3.15$	(1)	$k_{CT} = 8.70 (= k_{TC}K)$	(4)
$k_{TC} = 6.83 (= k_{TC}R_A)$	(2)	$k_{CT} = 18.66 (= k_{TC}R_AK)$	(5)
$k_{TT} = 8.16 (= k_{TC}R_{TT})$	(3)	$k_{CC} = 10.84 (= k_{TC}R_{CC})$	(6)

Definitions and Derivations

$K = k_{CT}/k_{TC} = k_{CT}/k_{TC} = 2.74$	(0.98 kcal/mol)	(7)
$R_A = k_{TC}/k_{TC} = k_{CT}/k_{CT} = 2.15_6$	(0.75 kcal/mol)	(8)
$R_{TT} = k_{TT}/k_{TC} = 2.59$	(0.93 kcal/mol)	(9)
$R_{CC} = k_{CC}/k_{TC} = 3.44$	(1.21 kcal/mol)	(10)

Figure 8. The experimental results and kinetic dissection of the thermal rearrangement of cis- and trans-1-cyano-2-isopropenylcyclopropane (cis-IV and trans-IV) in the gas phase at 217.8°, all rate constants in units of $(10^6 \text{ sec})^{-1}$.

three measurements ($k_{t,c} + k_{c,t}$) determined from either racemic trans or racemic cis and K independently, or from both trans and cis whereby K is determined concomitantly; and R_A from either optically active trans or optically active cis.

The crossed reactions, (—)-trans → (+)-trans and (+)-cis → (—)-cis, are enantiomerizations and must be determined separately. Their rate constants can also be expressed in terms of k_{TC} if it is desirable explicitly to call attention to the ease of these processes relative to the least favorable process, k_{TC}, in which R_B, the relative ease of the rotation of B, is implicitly equal to 1.

In these terms the experimental observations on cis- and trans-1-cyano-2-isopropenylcyclopropane are treated in the following manner (eq 15-17) where

$$R_A = R_{CN} = k_{TC}/k_{TC} = k_{CT}/k_{CT} \quad (15)$$

$$(k_{t,c} + k_{c,t}) = k_{CT} + k_{TC} + k_{CT} + k_{TC} =$$
$$k_{TC}[(R_{CN} + 1.00)(K + 1.00)] \quad (16)$$

$$R_{TT} = (k_\alpha)_T/2k_{TC} \text{ and } R_{CC} = (k_\alpha)_C/2k_{TC} \quad (17)$$

$(k_\alpha)_T$ and $(k_\alpha)_C$ are the specific rate constants for racemization of trans and cis, respectively.

The experimental results of Bergman and Carter[4] may also be presented in terms of this general scheme. Their emphasis on "the extremely complex" nature of the complete system and their conclusion that R_{Me}, the ratio of (+)-trans to (—)-trans from (—)-cis, was better neglected in order to make the system manageable, may have been unnecessary, but were not contrary to their purpose of subjecting the prediction of Hoffmann[9] to test. Since all the needed information is given in their

(−)-*trans* (T) (+)-*cis* (C)

(−)-*cis* (C) (+)-*trans* (T)

Experimental Results [temp = 407.95° (681.10°K)]

k_{TC} = 2.88	(1)	k_{CT} = 8.21 ($=k_{TC}K$)	(4)
k_{TC} = 3.38 ($= k_{TC}R_A$)	(2)	k_{CT} = 9.64 ($= k_{TC}R_AK$)	(5)
k_{TT} = 3.28 ($=k_{TC}R_{TT}$)	(3)	k_{CC} = 8.40 ($=k_{TC}R_{CC}$)	(6)

Definitions and Derivations

$$K = k_{CT}/k_{TC} = k_{CT}/k_{TC} = 2.85 \ (1.42 \text{ kcal/mol}) \quad (7)$$
$$R_A = k_{TC}/k_{TC} = k_{CT}/k_{CT} = 1.17 \ (0.22 \text{ kcal/mol}) \quad (8)$$
$$R_{TT} = k_{TT}/k_{TC} = 1.14 \ (0.18 \text{ kcal/mol}) \quad (9)$$
$$R_{CC} = k_{CC}/k_{TC} = 2.92 \ (1.45 \text{ kcal/mol}) \quad (10)$$
$$\log k_{TC} = 14.40 \pm 0.26 - (59022 \pm 677)/4.575T$$
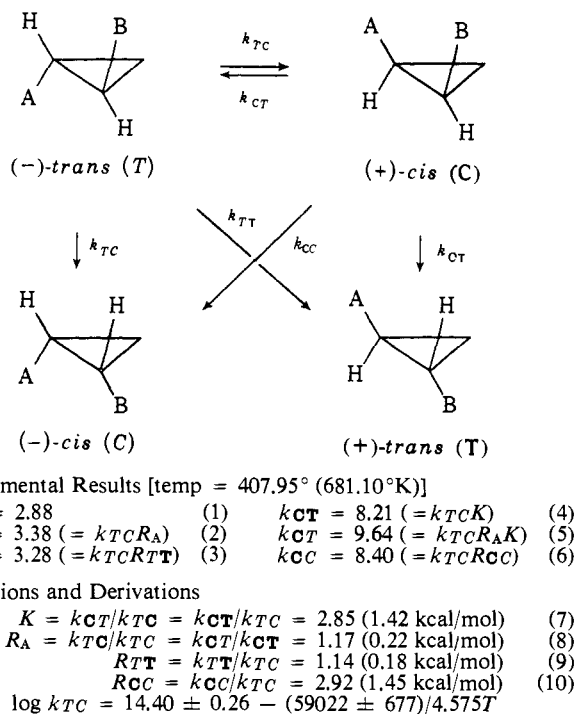
Figure 9. The behavior of *cis*- and *trans*-1-ethyl-2-methylcyclopropane taken from Bergman and Carter and recast in terms of the scheme for presentation of rotational preference (see text). R_A is the rotational preference of methyl (A) over ethyl (B) and specific rate constants are in units of (10^5 sec)$^{-1}$.

Table V. Recalculation of the Data of Bergman and Carter on the Thermal Reorganization of *cis*- and *trans*-1-Ethyl-2-methylcyclopropane[4]

Temp, °K	k_{TC}, × 10^5 sec^{-1}	R_{Me}	R_{TT}	R_{CC}	K^a
650.36	0.368		1.035	2.516	2.955
677.46	2.309	1.174	1.165	3.114	2.865
694.26	6.327		1.252	3.054	2.810
711.86	19.376		1.112	2.990	2.751

a Values of K calculated from the data of Elliott and Frey.[2e]

paper, their data are recast in Table V into the four-component scheme by means of the eq 18 where R_{Me} =

$$k_{TC} = k_i(R_{Me} + 1)(K + 1) \quad (18a)$$

$$k_{CC} = [k_r - k_{TC}K(R_{Me} + 1)]/2 \quad (18b)$$

$$k_{TT} = [k_r' - k_{TC}(R_{Me} + 1)]/2 \quad (18c)$$

1.17 and k_i, k_r, and k_r' are taken from their paper,[4] and k_r, defined by Bergman as loss of optical activity in the entire mixture of rearrangement products, is set equal to $k_{CC} + k_{CT} + k_{CT}$. The other terms are defined in Figure 9. Since the accuracy of measurement of the optical activity may correspond to an error in excess of enantiomer of possibly ±1% out of a total of 8%, an estimated error in R_{Mc} of ±0.03 is reasonable.

In terms of 180° rotations of groups, diastereomerization is achieved by an odd number of rotations, whereas enantiomerization is achieved by an even number of rotations. The odd number of rotations leading to diastereomerization is composed of an odd number of rotations of one group and an even number of rotations of the other group. Which enantiomeric diastereomer

is produced depends on which group rotates the odd number of times. Thus, an odd number of rotations of the cyano group (the major process by 68.4%) transforms (C) into (T) (or (T) into (C) the major process by 68.2%), whereas an odd number of rotations of the vinyl group (the minor process by 31.6%) transforms (C) into (T) (or (T) into (C), the minor process by 31.8%).

Enantiomerization is expressed as an even sum of a pair of odd series. An even sum resulting from a pair of even rotations is the equivalent of no change.

One of the two sets of rotations for achieving an overall odd number of rotations and for achieving an overall even number of rotations are

even vinyl:	0	2	4	6	...
odd cyano:	1	3	5	7	...
odd sum:	1(1) 3(2)	5(3) 7(4)	9(5) 11(6)	13(7)	...

where the sum, achievable by n different combinations of 180° rotations, is $2n - 1$ where $n \geq 1$ and

odd vinyl:	1	3	5	7	...
odd cyano:	1	3	5	7	...
even sum:	2(1) 4(2)	6(3) 8(4)	10(5) 12(6)	14(7)	...

where the sum, achievable by n combinations, is $2n$ where $n \geq 1$.

Any reaction the structural course of which can be formulated as the breaking of an sp^3–sp^3 carbon–carbon bond and the remaking of the same sp^3–sp^3 carbon–carbon bond, can lead to a maximum of three configurational isomers (excluding the starting material as the fourth).

The present investigation is the first explicit example of a general method for determining the relative ease of 180° rotations by different groups. Rotational preference is the decisive factor in determining which enantiomer is favored in diastereomerization consequent to opening and reclosing a ring. Whether molecular weight, shape, or other constitutional, configurational, and physical properties are the significant determinants of this rotational factor is not known, but a method of study is now clearly delineated.

Further studies of the type of "closing the circle" can be visualized in which, for example, R_A of this work [rot(CN)/rot(iPr)] may be combined with R_A from 1-cyano-2-phenylcyclopropane [rot(CN)/rot(Ph)] to furnish a predicted value for R_A [rot(Ph)/rot(iPr)] which may be compared with an experimental value obtained from 1-isopropenyl-2-phenylcyclopropane. In this manner, gradually, it could be ascertained to what extent propensity to engage in the rotational act might be an intrinsic attribute of a group. Another peal on the bells of physical organic chemistry is there for the ringing.

A recent investigation by Chmurny and Cram[34] includes the thermal rearrangement of optically active 1,2-diphenylcyclopropane-1-carboxylate and contributes to the elucidation of rotational propensity. Their results, phrased in terms of Figure 9 in which "(+)-*cis* (C)" is replaced by "(+)-(E)-1," are, at 457.52° K, k_{TC} = 0.85 × 10^{-6} sec^{-1} [(−)-(Z)-1 → (−)-(E)-1], K = 0.52, k_{TT} and k_{CC} are unobservably small, and

(34) A. B. Chmurny and D. J. Cram, *J. Amer. Chem. Soc.*, **95**, 4237 (1973).

$R_A = 13.3$. Two emergent hypotheses may be further explored: that the presence of two sterically large groups on one carbon atom decreases its propensity to undergo internal rotation alone, or even more strikingly, in conjunction with the rotation of the second atom.

At this moment knowledge of rotational propensities (R_A) in cyclopropanes is limited to three comparisons.

$$\text{methyl-hydrogen/ethyl-hydrogen} = 1.17^4$$

cyano-hydrogen/isopropenyl-hydrogen =

$$2.15 \text{ (this work)}$$

$$\text{phenyl-hydrogen/phenyl-carbethoxy} = 13.3^{34}$$

Concerted Mechanisms

These nitriles undergo as their most prominent thermal rearrangement, a pair of cis-trans geometrical isomerizations which require an odd number of formally 180° rotations and, seemingly inescapably, an orthogonal relationship between the two participating carbon atoms at some point during the rearrangement. At that point bonding between the atoms essentially vanishes and the rearrangements may be considered to be not concerted. Nonetheless, the total number of rotations must be small, otherwise the resultant diastereomer would be racemic.

The third, less prominent rearrangement, enantiomerization, requires an even number of rotations and can in principle be concerted. Suffice it at this point in the development to emphasize that the magnitude of the concert is sufficiently small to confer no discernible advantage on that path.

The history of internal rotations in the thermal behavior of cyclopropane begins with the discovery by Rabinovitch, Schlag, and Wiberg[2a] of the formally single-rotational process required to effect geometrical isomerization (diastereoisomerization) in 1,2-dideuteriocyclopropane. Further examples, including that of a vinylcyclopropane,[2g] have been uncovered.[2]

About 5 years ago, the formally double-rotational process of enantiomerization (racemization) was discovered by Crawford and Lynch,[3a] Berson and Balquist,[3b] and Carter and Bergman[4] by the introduction of optical activity and Willcott and Cargle[2h] by the introduction of an additional prochiral center (a 3-vinyl group into 1,2-dideuteriocyclopropane).

These works provided an effective test of the theoretical prediction of Hoffmann[9] that the favored reaction would involve a "π-cyclopropane," "0,0-planar diradical" intermediate station, arrived at and departed from by synchronous conrotatory motions, and that the single rotation required to effect diastereoisomerization would be disfavored by a barrier predicted to be 10 kcal/mol. The experimental tests are all in agreement that there is no striking kinetic preference for enantiomerization over diastereoisomerization. The present work, although even further removed from the ideal substrate, optically active trans-1,2-dideuteriocyclopropane, nonetheless provides another example of failure to observe the preference predicted by Hoffmann: no more than 46% of the reorganization of (−)-trans-IV (the portion rearranging to (+)-trans-IV) or 28% of the reorganization of (+)-cis-IV (the portion rearranging to (−)-cis-IV) involves the Hoffmann-favored path. How this

theoretically based prediction went so wrong deserves an early explanation.

In a calculation of imposing proportion,[10] Salem has identified the path of minimum energy in the geometrical rearrangement of cyclopropane to be an extension of the bond, as hypothesized earlier by several workers, followed by a rotation of one atom aided by a slight simultaneous rocking of the other until a zero-bonded orthogonal transition state is reached. The completion of the process is the reverse of the first half. The predicted activation energy for this path for diastereomerization is 52.6 kcal/mol, while that for enantiomerization is 52.0 kcal/mol. In fact, (−)-trans-IV reorganizes to the diastereomers to the extent of 54% (37% to (+)-cis-IV by cyano rotation and 17% to (−)-cis-IV by isopropenyl rotation) and to enantiomeric (+)-trans-IV to the extent of 46%. Agreement with the predictions of Salem and his coworkers, 35 and 65%, respectively, is excellent. The reorganization of (+)-cis-IV leads to the diastereoisomers to the extent of 72% (49% to (−)-trans-IV by cyano rotation and 23% to (+)-trans-IV by isopropenyl rotation), while the remaining 28% is the enantiomerization to (−)-cis-IV.

Mechanisms with Common Intermediate

A common intermediate such as the widely supported diradical, trimethylene,[35] can be excluded from a major role in the thermal behavior of 1-cyano-2-isopropenylcyclopropane. The persistence of significant amounts of optical activity is itself incompatible with an exclusively common intermediate. The greater the contribution of an intermediate common to both (−)- and (+)-trans-IV, the more would R_A, which is also the measure of the retention of optical activity, tend toward 1.000. The experimental value of 2.15 is equivalent to a maximum contribution of 63% of a racemic common intermediate [$f_{rac} = 2/(R_A + 1)$]. This criterion of commonality of intermediate is absent from the previous studies of the stereochemistry of the cyclopropane rearrangement[2,3] owing to the achirality of the cis diastereomer. The exception as stated before is the example of Bergman and Carter[4] where the presence of two different substituents, methyl and ethyl, makes provision for the operation of the criterion, but their near-identity leads to such a small discrimination (8% of retention of optical activity) that as much as 92% of the reaction is permitted to proceed by a common achiral intermediate. In the recent example of Chmurny and Cram[34] the high value of $R_A = 13.3$ permits no more than 14% involvement of a common achiral intermediate. It remains to be seen to what extent different choices of A and B may influence the manifestation of the criterion.

Another approach to the assessment of commonality of intermediate involves examination of the independent cross reactions: the rearrangements of (+)-cis to (−)-cis and (−)-trans to (+)-trans.

When all four products are being produced from a common intermediate, the total rate of reaction of (+)-cis and (−)-trans may be factored into four parts corresponding to the rates of formation of −T (T), +T (T), −C (C), and +C (C) (eq 19). From the definition of K

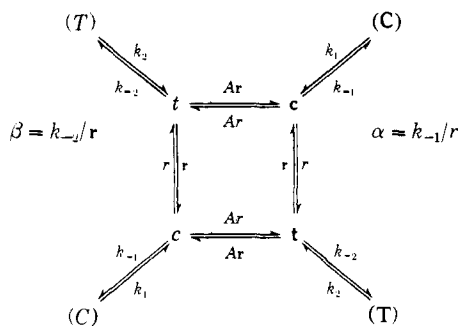(35) M. C. Lin and K. J. Laidler, Trans. Faraday Soc., 64, 927 (1968).

Figure 10. Model for mechanism with diradical intermediates interconnected by single rotations. T, C, **T**, and C defined in Figure 8; t, c, t, and c being the related diradicals.

$$\frac{Kk_{TC}\left(R_A + 1 + 2\dfrac{R_{CC}}{K}\right)}{k_{TC}(2R_{TT} + 1 + R_A)} \quad (19)$$

and application of the principle of microscopic reversibility, the ratio of these total rate constants must equal K when the products are joined by a common intermediate. Not only does this condition require that the two terms within parentheses in (19) be equal, but that the rate constants for formation of individual products from this common intermediate be independent of the origin; that is, the individual expressions of (20) must hold. A

$$R_A = R_{TT}$$

$$1 = R_{TT}$$

$$R_{CC}/K = 1 \quad (20)$$

$$\frac{R_{CC}}{K} = R_A$$

solution exists only when each of the individual terms equals 1. The maximum allowable contribution of a common intermediate may then be calculated: 71% in the reaction of cis and 47% in the reaction of trans. In the Bergman–Carter example, the corresponding values, 95% for cis, 90% for trans, are higher. The contribution from a component not-in-common in the present instance is too large to be treated as a minor neglectable aberration.

Since the number of independent observables is just equal to the task of evaluating the relative rate constants of formation of the three products, none is left over to illuminate the many degrees of freedom which take the form of mechanistic hypotheses. Thus, arguments in respect of the hypothesis of a common intermediate take the following form. If it be assumed that the observational device is suited to the detection of a common intermediate, then observations already made place the following maximum limits on the amount of common intermediate: 63% in respect of retention of optical activity; 47% in respect of the production of (+)-trans from (−)-trans.

Among various detailed hypotheses for the "common intermediate" is a square array of diradicals each interconvertible into an adjacent neighbor by internal rotations, but not directly convertible into an opposite neighbor without stopping at an adjacent way station (see Figure 10). Retention of optical activity ($R_A > 1$) precludes the "rotational" rate constants for moving about

the array (**r**, r and A**r**, Ar) being large compared to the "cyclization" rate constants for getting off the array (k_{-1} and k_{-2}); or stated in terms of the 180° rotations needed to produce the three products, the sums of these rotations may not be large. A similar initial exclusion follows from the fact that the ratios of the rates of formation of (**T**) and (C) from (T) (2.59) and of (C) and (**T**) from (**C**) (1.25) are not equal.

In terms of this hypothesis it is equally clear that getting off the array (k_{-1} and k_{-2}) is not permitted to be much faster than moving around the array, for then (**T**) would not be formed directly from (T) [nor (C) from (**C**)] (see Figure 10).

The possibility that the experimental ratios of initial rate constants may be accommodated within this mechanistic hypothesis by suitable adjustment of the available parameters can be explored. (The rest of this section attempts to show such an accommodation is not possible within acceptable limits and may be treated as an appendix by proceeding to the next section.) By means of the usual approximations of the steady state, equations for the concentrations of the four intermediates may be written. When (T) [or (**C**)] is the starting material and initial rates are being sought, the rates of the three reverse reactions (e.g., $k_1[(C)] + (C)] + k_2[(T)]$) are zero. From four equations of the sort (eq 21) for the steady-state concentrations, where $P =$

$$t = [k_2[(T)] + r(c + Ac)]/P$$

$$c = [r(t + At)]/Q \quad (21)$$

r($\beta + 1 + A$) and $Q = r(\alpha + 1 + A)$, four equations in terms of the specific rate constants of the hypothesis may be derived: one set (eq 22) starting from (T),

$$t = M2AQ/rY, t = MQZ/rY,$$

$$c = MA(Z + 2)/Y \text{ and } c = M(Z + 2A^2)/Y \quad (22)$$

where $M = k_2[(T)]/r$, $Y = Z^2 - 4A^2$, and $Z = (PQ/rr) - 1 - A^2$; and another set (eq 23) starting from **C**,

$$t = N(Z + 2A^2)/Y, t = NA(Z + 2)/Y,$$

$$c = NPZ/rY \text{ and } c = N2AP/rY \quad (23)$$

where $N = k_1[(C)]/r$.

From these equations, expressions for the ratios of any of the experimentally determined, initial rates may be set down. For example, x, the ratio of the crossed

$$x = \frac{k_{CC}}{k_{TT}} = \frac{\alpha}{\beta}K\frac{k_{-1}P}{k_{-2}Q} = K\left(\frac{\alpha}{\beta}\right)^2\frac{\beta + 1 + A}{\alpha + 1 + A} = 1.328 \quad (24)$$

$$K = \frac{k_1Ark_{-2}}{k_2Ark_{-1}} = 2.74$$

$$y = R_A = A\frac{Z + 2}{Z + 2A^2} =$$

$$A\frac{\alpha\beta + (\alpha + \beta + 2)(1 + A)}{\alpha\beta + (\alpha + \beta + 2A)(1 + A)} = 2.155 \quad (25)$$

$$z = \frac{k_{CT}}{k_{CC}} = \frac{k_{-2}Z + 2A^2}{\alpha \quad 2AP} =$$

$$\frac{\beta}{\alpha}\frac{\alpha\beta + (\alpha + \beta + 2A)(1 + A)}{(2A)(\beta + 1 + A)} = 0.803 \quad (26)$$

enantiomerizations (eq 24), y, the ratio, R_A, defining the

rotational preference (eq 25), and z, the ratio of the rate of diastereomerization of (C) to (T) and the rate of enantiomerization of (C) to (C) (eq 26), can be described in terms of $\alpha = k_{-1}/r$, $\beta = k_{-2}/r$, and A (see Figure 10).

The problem is to solve the three simultaneous equations in α, β, and A. Each equation has its own surface of solutions in three-dimensional space, while any two will have, as a line of solutions, the intersection of the two surfaces. A simultaneous solution exists if this line of solutions intersects the third surface.

Rearrangement of the expression for x gives eq 27 from

$$\frac{\beta}{\alpha} = \sqrt{\frac{K}{x}} \sqrt{\frac{\beta + 1 + A}{\alpha + 1 + A}} \qquad (27)$$

which it is clear that the ratio of the crossed reactions is overwhelmingly determined by the ratio, β/α. Since $(K/x)^{1/2} = 1.44$ in the present instance, it follows that $\beta/\alpha \geq 1.44$ regardless of the value of A.

The equation for R_A may be rearranged to the form in eq 28 from which it is clear that A must be greater than

$$\frac{\alpha\beta}{1 + A} + (\alpha + \beta) = 2(R_A - 1)\frac{1}{1 - R_A/A} \qquad (28)$$

R_A or 2.155 at all times. It may also be rearranged to the form in eq 29 where $R_A/A = D$. The surface of solu-

$$\alpha = \frac{2(A + 1)(AD - 1) - \beta(A + 1)(1 - D)}{(1 - D)(\beta + A + 1)} \qquad (29)$$

tions of the equation y for R_A (eq 25) was sketched in for values of A ranging from 4.00 to ∞. The same was done for the equation x (eq 24) and z (eq 26). The intersection of these surfaces with the surface of solutions of y each gives a line of solutions. These two lines come closest to an intersection at $A = \infty$ and diverge for lower values of A. Even at $A = \infty$, only a small part of the experimental behavior is accommodated. Thus, a common solution at $A = \infty$ would involve $x = 4.08$ instead of its experimental value of 1.328. Phrased another way, if at that point k_{CC} were to be fixed at its experimental value of 10.84×10^{-6} sec^{-1}, k_{TT} would have to be 2.66 for a complete representation of the system. Since its actual value is 8.16, 67% of this reaction is not accounted for by the best adjustment of the parameters. The situation becomes even worse if a lower, more reasonable value of A is selected.

The Diradical as Transition State.
A Continuous, Nonconcerted Model

Rather than retain the common intermediate in one of its various forms and be obliged to add to it another mechanism of comparable importance or construct a combination of a concerted, birotational mechanism in relatively ineffective competition with a nonconcerted mechanism, we prefer to work within a conceptual scheme energetically related to the concept of a nonconcerted diradical mechanism but dynamically continuous without the time-dependent characteristics of two-step mechanisms *cum* intermediate. This picture departs from the commonly accepted picture of a singlet diradical as intermediate.[35]

This scheme pictures each of the three processes leading to the enantiomer of the starting material and the two enantiomeric diastereoisomers to be variations of a single type of continuous process. The scheme is based
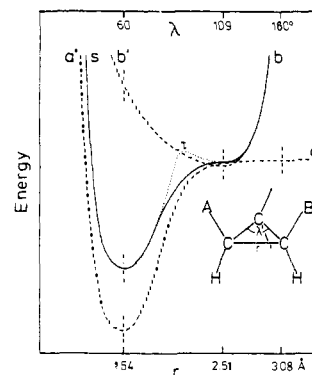
Figure 11. A representation of the relationship of distance of separation, r (and the subtended angle, λ), between two carbon atoms of cyclopropane and energy. Curve a–a' is of the Morse-type between energy and distance of separation (r) in an acyclic carbon–carbon bond. Curve b–b' represents the change in energy with the angle λ in an acyclic model such as propane. The superposition of these two curves generates the "stretching–bending" mode in cyclopropane, the curve s–b. The maximum, τ, results when curves are displaced, b–b' to the right and a–a' to the left, respectively.

on the model underlying the Rice–Ramsperger–Kassel–Marcus theory of unimolecular reactions. As much as possible, terminology is that employed in the superlative monograph of Robinson and Holbrook.[36] The conceptual scheme for unimolecular ring opening is given in some detail in order to make unambiguous the distinctions between concerted and continuous, and between diradical as intermediate and the diradical as the appropriate model for the theoretical estimation of activation energy.

The greater fraction of the activation energy is pictured concentrated in upper levels of stretching vibrational modes at the outer extensions of which the distance of separation is comparable to that in the ground state bending vibrational level of a hypothetical diradical (that is, in the normal bending mode of a methylene group). This distance of separation (>2.5 Å) is considered too great for any significant residual covalent bonding or orbital overlap in terms of the Hückel model.

A simple model for the bond-breaking process in cyclopropane or other small rings may be visualized as shown in Figure 11 as the superposition of a Morse-like curve (a–a') for carbon–carbon bond stretching and a curve (b–b') representing the CCC bending vibrational mode of the central methylene group as in propane. This mode reaches its peak far off the diagram at 180° and 3.08 Å in the square planar geometry associated with the unknown thermal inversion of an sp^3 carbon atom.[37]

If states of negligible bonding between the two carbon atoms define a "singlet diradical," that is, states having energy greater than that of level a, then the "singlet diradical" becomes an intermediate when there is a

(36) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions," Wiley-Interscience, London, 1972.

(37) Since this discussion, to be anything but the first approximate step away from the customary one-dimensional "reaction coordinate," should more properly be in n-dimensional space, other dimensions would need to be introduced to reflect other possible escapes such as H migration to give propene or elimination of a carbene to produce an olefin. To introduce the fewest complications consistent with illustrating the conceptual scheme we have stayed with a description of the reaction in three dimensions (four including energy).
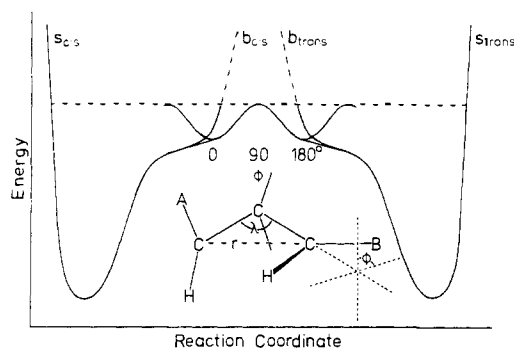
Figure 12. A representation of the single torsional linkage between the "stretching–bending" modes of two diastereomers: for example, cis on the left ($\phi = 0°$) and trans on the right ($\phi = 180°$). The left- and right-hand curves are of the b–s type from Figure 11 linked by the internal rotation of one radical carbon atom *vs.* a second, which is considered nonrotating in this particular figure.

maximum in the composite curve s–b between the 60°/1.54 Å point and the 109°/2.5 Å point. Such a situation can obtain if the energy of the angular compressional curve (b–b') increases faster than the energy of the bonding curve (a–a') decreases; the resultant can then be the barrier essential to the existence of an intermediate (the point τ of Figure 11).[38]

If there is no subsidiary maximum, there will be no intermediate diradical. This situation, curve s–b in Figure 11, is insignificantly different from the normal stretching–vibrational curve in its lower energy levels and would ordinarily culminate in bond dissociation were the bond not part of a ring. But at levels of energy equal to or higher than those sufficient to break an acylic bond [greater than level a], the covalent bond of the ring is restrained from breaking into two pieces by the resistance of the methylene group to attaining the square planar state. A vibrational mode which is adequately described as a bond-stretching mode at its lower energy levels becomes a bending mode in its upper reaches. At energy level a or higher this situation corresponds to a diradical only in the sense that an acylic bond would now be broken into two radicals.

At no point is it useful to describe the system as a diradical, if by that description is meant a barrier-protected diradical on which further reactions or applications of activation energy can be imposed. In

(38) It may be noted that the activation energy for reaching the diradical may not be *less* than the difference (55 kcal/mol) between the C–C bond strength (82 kcal/mol) and the strain of cyclopropane (27 kcal/mol). As suggested by Benson[39] to explain the 64 kcal/mol activation energy for cis–trans isomerization,[2a] the curve for "breaking" the bond in cyclopropane should have an energy of activation corresponding to an unprecedented activation energy of 9 kcal/mol for reclosure (as in the right-hand diagram of Figure 11). Even such stabilized radicals as allyl seem to recombine without an activation energy, following a simple Morse curve.[27] In cyclopropane it would be hypothesized that the boundaries of the bending vibrational mode are encountered *before* (in terms of distance separating the two atoms) covalent bonding can become the dominant, more than compensating, energetic factor. For what it may be worth, neither theoretical calculation has turned up the Benson barrier.[9,10] We suspect that the thermodynamically derived strain energy should have been placed on the same scale as the *low-pressure* limiting activation energy and not on the scale of the conventional *high-pressure* limiting activation energy. A difference of 9 kcal/mol between these two activation energies is not unreasonable[40] and would completely encompass the "Benson activation energy." Alternatively, see the analysis of "Benson strain" given by G. R. Freeman, *Can. J. Chem.*, **44**, 245 (1966).

(39) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

(40) See, for example, K. A. Holbrook, J. S. Palmer, K. A. W. Parry, and P. J. Robinson, *Trans. Faraday Soc.*, **66**, 869 (1970).

cyclic compounds, "diradical" corresponds to vibrational levels of the molecule with energy greater than that corresponding to a pair of radicals. In terms of the RRK model, these stretching-bending levels may be transformed into other internal vibrational modes with or without the intercession of external collisions.[36] It is useful to speculate that the energy of the levels at which the amplitude of the "stretching" mode changes to the markedly greater amplitude of the "bending" mode is approximated by the energy the diradical would have had if the distance separating its two atoms had been infinite.

At this point in the development, it should be iterated that the accumulation of energy in the "stretching-bending" mode, even of large excesses of energy, of itself leads to no reaction. Redistribution into other modes can of course lead to numerous other reactions.[37]

There is a question of "concertedness." Vibrations regardless of energy levels are dynamically, classically mechanically "concerted" processes in such an obvious sense it were better to describe them as "continuous" processes were there any call for a description. At the "diradical" vibrational levels, the amplitude is so great that exceedingly strong overlap or bonding characterizes the compressional side and essentially no overlap or bonding, the extensional side. At these distances of extension, concertedness or control by first-order orbital overlap in terms of Woodward and Hoffmann[23] or Berson and Salem[24] becomes vanishingly small and, in no event, can the free energy of control exceed the value of residual bonding at the outer extension of the vibration. The vibration nonetheless remains a completely continuous process. In terms of the identification of "diradical" with vibrational levels high enough to be described as "stretching-bending" modes, the compressional phase of the vibration can also be described as the combination of two radicals to produce a covalent bond or the trapping of one radical by another. This process, so well known in conventional systems of radicals as the recombination of two radicals, is subsumed in the cyclic cases within the set of "stretching-bending" vibrational modes.

The nonreacting "diradical" levels of the "stretching-bending" modes may become reacting modes when torsional or internal rotational modes are superimposed on the "diradical" modes. The extra energy required is presumed to be comparable to that required for rotation in the related acylic radical. This energy is added to the energy required to reach the "diradical" levels of the "stretching-bending" mode. It is for the purposes of developing the conceptual scheme that we feel justified in dissecting normal vibrational modes into hypothetical component parts in the fashion of the organic chemist treating infrared frequencies. At the outer extension of the "stretching-bending," a simultaneous internal rotation of one carbon atom as far as 90° allows the compressional phase of the mode to enter a new diastereomeric configuration (see Figure 12). At this point, orthogonality is added to excessive distance as the destroyer of residual bonding and the possibility of Hückel overlap. This geometry more or less approximates the transition state favored by Salem[10] and calculated by Hoffmann[9] to be disfavored by 10 kcal/mol.

There are three families of vibrations each consisting of large numbers of combinations of the "stretching-

bending" modes and the internal rotational modes at suitable total energy levels and each bringing the assembly of atoms at their outer extensions to a point where the instantaneous geometry is in common with, or reversibly derivable from, two different stable configurations of the assembly. Two major families involve single rotations of either the carbon atom, in the present instance, bearing the cyano group or the carbon atom bearing the isopropenyl group and are each divided into observationally indistinguishable clockwise and counterclockwise subfamilies. The third family involves the rotation of both carbon atoms simultaneously and is divided into conrotatory and disrotatory subfamilies, which, although without observational significance in simple cyclopropanes, have been the object of extensive theoretical treatment.[9] It is central to this conceptual scheme that, in any displacement from the point of maximum energy, only positive bonding will result (regardless of any residual bonding; i.e., the energetic possibility of concertedness; van der Waals attractions, steric interactions, hyperconjugation, and the other factors involved in the theoretical calculations of the energy of the system at this arrangement of the nuclei). This property describes a transition state even in the extreme instance where its energy is best approximated by the noninteracting diradical as model.

In the RRK model, the $3n - 6$ normal vibrational would be collected into the "stretching–bending" cum "single torsion" class and the "stretching–bending" cum "double torsion" class. Each mode among these classes (the "reacting" classes) is in theory subject to theoretical calculation of its energy levels and identification of the critical energy and dimensions at which point it achieves its role as activated complex and "diradical cum torsion." The ratios of products would then be determined by the ratios of the sums of level densities above critical energies for each member of the family. At infinitely low pressure, the ratio of products is determined by the differences in low pressure critical energies of the most favorable members of each family of reaction paths.

A question about the number of rotations involved in each product-determining act follows from the analysis given earlier of the number of rotations associated with each of three reactions. For example, it can be asked of any member of the family of paths resulting in the most favored reaction (the "monorotational" diastereoisomerization by rotation of the cyano group) whether the act involves only one actual rotation or some larger odd number (even numbers being fruitless). This question is significant in terms of hypothetical schemes involving the diradical as an intermediate and receives the answer: "The number of rotations imposed subsequent to the generation of the diradical must be small." The question loses its significance when the activated complex in its lowest, critical energy is reached. At this point in a grossly formal sense, two "diradicals" as upper energy levels of the "stretching" modes combined with the "bending" modes (Figure 11) merge through one of the four sets of torsional modes into a new vibrational mode encompassing both enantiomers or both enantiomeric diastereomers. As illustrated in Figure 12, the vibrational mode interlinking the two enantiomers or diastereomers shares in its upper levels the compressional boundaries of the individual configura-
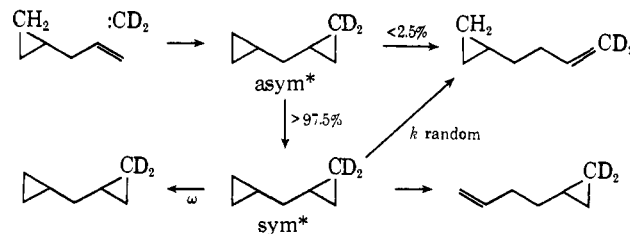

Figure 13. Symmetrization of energy in initially unsymmetrically chemically energized dicyclopropylmethane.

tions. In principle, the question, "How many rotational acts are involved?" is identical with the question, "How many vibrational lifetimes may the system spend in this particular energy level of this vibrational mode before redistributing its energy among some other one of the enormous number of equienergetic combinations available in all but the simplest organic molecules, the overwhelming majority of these combinations being inactive in terms of observable reaction consequences?"

In a series of remarkable "nmr determinations of barriers to internal rotation in halogen-substituted ethenes," Newmark and Sederholm have accumulated strong evidence "that deactivation of the rotational mode occurs in a time comparable with the rotational frequency."[41]

In the RRK model, flow of energy from one vibrational state to another is fast. The experimental evidence has been brought together by Robinson and Holbrook[36] and may be augmented by mention of a newer application of chemical activation to this question. By the addition of methylene to appropriately substituted olefinic cyclopropanes, a symmetrical product with two cyclopropane moieties can be generated with an initially grossly unsymmetrical distribution of excitation energy far in excess of that required to effect the cyclopropane–propylene rearrangement.[42] In a recently completed illustration,[43] 3-cyclopropylpropene is allowed to react in the gas phase with dideuteriomethylene (from dideuteriodiazomethane). At low pressure (low rate of collisional deactivation), rearrangement product, 4-cyclopropylbutene-1, can be isolated and analyzed for distribution of deuterium (see Figure 13). After correction for a small isotope effect (reaction of methylene with 3-(2',2'-dideuteriocyclopropyl)propene), statistical distribution within 2.5% is established.[43,44] Flow of energy away from its initial site must be much faster than rearrangement. Since rearrangement product can only be detected at low total pressure, the complete dynamic picture includes (a) generation of initially asymmetrically excited product, asym*, from which negligible nonrandom rearrangement originates, (b) rapid flow of energy into nonreactive modes, sym*, (c) slow remobilization of energy into modes appropriate to rearrangement (k random) and (d) continuously competing collisional deactivation, ω, to unrearranged addition product. In the context of

(41) R. A. Newark and C. H. Sederholm, J. Chem. Phys., **43**, 602 (1965).

(42) W. von E. Doering, J. C. Gilbert, and P. A. Leermakers, Tetrahedron, **24**, 6863 (1968).

(43) N. L. Avery, III, "Intramolecular Energy Relaxation in Asymmetrically Activated Molecules," Ph.D. Dissertation, Harvard University, Feb 1972 (Diss. Abstr., **33**, 105-B (1972)).

(44) For a similar study, see J. D. Rynbrandt and B. S. Rabinovitch, J. Phys. Chem., **74**, 4175 (1970); **75**, 2164 (1971).

Table VI. The Effect of Phase and Pressure on the Rearrangement of 1-Cyano-2-isopropenylcyclopropane at 217.8°

Starting material	Phase	Rac. in rec. starting material, %	Product,			Time, min
				%	$[\alpha]^{28}$D	
(+)-cis-IV	Gas 1 mm	17.5	trans-IV		−66.3[a]	150
(+)-cis-IV[c]	Gas, 600 mm	15.5	trans-IV	22.5	−65.8[a]	150
(+)-cis-IV	Benzene (6%)	10.7	trans-IV	19.3	−64.5[a]	150
(−)-trans-IV	Gas, 2 mm	27.5	cis-IV		−58.3[b]	310
(−)-trans-IV[c]	Gas, 600 mm	25.5	cis-IV	13.05	−57.7	310
(−)-trans-IV[c]	Gas, 600 mm	19.8	cis-IV	10.17	−62.1	220
(−)-trans-IV	CH₃CN (7%)	13.5	cis-IV	9.9		220

[a] Corrected to 100% optical purity of starting (+)-cis-IV. [b] Measured on a sample of trans-IV obtained by epimerization of cis-IV in the usual manner and corrected to −203.4°, $[\alpha]^{28}$D of pure (−)-trans-IV, as the specific rotation of starting material. [c] These experiments are repeated from Tables II and III to facilitate comparison.

this dynamic reaction scheme, it is particularly relevant to the present work that no trans-1,2-dimethylcyclopropane is obtained from the reaction of cis-butene and methylene at higher pressures; that is, the nonrandom component of cis–trans geometrical isomerization of excited cis-1,2-dimethylcyclopropane is also negligible.

The answer to the question, "For how many vibrational lifetimes does the activated complex (in more conventional situations, the reaction coordinate) survive as a reversible reaction?", is not very many and unlikely to be more than one.

Such detailed, extensive concern with the question is justified by its relevance to the related question: "How long can a hypothetical classical singlet diradical survive as an intermediate?" Each time the two partners of the diradical come within bonding distance, trapping by covalent bond formation will occur immediately and essentially irreversibly on the time scale of molecular vibrations owing to the extreme rapidity with which the initially localized energy of bond formation necessary and sufficient to bond breaking is rapidly dissipated by distribution among other, nonactive modes. The larger the number of atoms, n, in the molecule, the more nearly true this statement is even at the lowest pressures; while the smaller the value of n the more nearly will the conclusion be false and simultaneous bimolecular, energy-dissipating collision will be required to make it true. This self-quenching potential in larger molecules is the dominant factor in determining the role of singlet diradicals as intermediates. The best trap for a diradical is its own reclosure to a covalent bond. That this trap operates effectively in the present example of a cyclopropane containing two radical-stabilizing, strain-unaltering substituents is the most important conclusion to be drawn from these present experimental results. The enthalpy of activation for its operation is apparently zero over a wide range of stabilizing substitutions and over the opposition of the strain in three- and four-membered rings; the contribution of "entropy of activation," the $-T\Delta S^{\ddagger}$ term, for the operation of the trap may range from infinite (in outer space) when two radicals of acyclic origin are involved, to zero in the geometrical isomerization of olefins and three-membered rings. It probably has intermediate values of increasing magnitude as the diradical configurations are derived from large rings and possess minima in the torsional profile at which interaction between the two diradicals is negligible.

Whereas it has been adequate to consider the mechanism, or the transition state, for a reaction, as molecules become more complicated than hydrogen, the

bond-breaking process may need to be viewed as a family of individual processes, the number of which increases with the complexity of the empirical formula and decreases in response to certain symmetry elements in the molecule. In general, the mechanism of the reaction then consists of the sum of many individual paths each of which contributes in proportion to its critical energy and entropy. In most dissociative reactions, remembrance of the initial states of radicals is lost so quickly that it is operationally superfluous to consider all the members of the family and it is justified to speak of a single mechanism in which the bond breaks to a pair of radicals.

In all processes dependent on breaking and re-forming the bond of a ring, internal rotation of some sort is an essential element. As a continuous element, it is totally dominant in the thermal geometrical isomerism of an olefin,[45] a major factor in configurational isomerizations of three-membered rings, and probably still important in isomerizations of four-membered rings. However, in bond breaking in large rings, the acyclic model (that is, the production of a diradical intermediate in which the two parts behave independently of each other) is probably satisfactory, but this point requires further exploration and definition.

Effect of Pressure on Lifetime of Energized Molecule

The effect of pressure has been examined in order to determine whether a change in the lifetime of the active molecule (the energized molecule, the molecule containing the requisite activation energy) alters the course of the rearrangement. The results of several experiments are given in Table VI. This examination has not extended into the very low pressure region where an effect of still energized products of rearrangement[46] or the effect of pressure lowering on the activation energy might be discerned. Were the abandoned and unsatisfactory scheme of a diradical intermediate on a square array to be operating to a significant extent, it is possible that a marked increase or decrease in the rate of collisional deactivation might change the values of α and β (see Figure 10) and thus the experimental ratios among the three reaction products. Reduction of the pressure from 500 to 1–2 mm occasioned no change within experimental error in the rate of racemization of starting material, the rate of formation of diastereomer, or the distribution of enantiomers within

(45) H. M. Frey, Proc. Roy. Soc., Ser. A, 251, 575 (1959); D. W. Setser and B. S. Rabinovitch, Can. J. Chem., 40, 1425 (1962); J. Amer. Chem. Soc., 86, 564 (1964).

(46) M. C. Lin and K. J. Laidler, Trans. Faraday Soc., 64, 94 (1968).

it. More significant is the absence of any major effect on passing from 500 mm to benzene solution ("infinite" pressure). Although a slowing of all rates by 30% may be experimentally significant, the ratio of (−)-trans-IV to (+)-trans-IV from (+)-cis-IV remains about the same as before. The experimental retention of optical activity (−62.1°) is corrected for the optical purity of the starting material (0.963) and for the 10.7% racemization in recovered (+)-cis-IV [(1.000 − 0.107/2) is taken as an approximate correction factor]. The derived value of R_A (2.01) may be compared with the gas-phase value (2.15). It is concluded that collisional deactivation is not a factor in determining the relative rates among the three rearrangements.

It was found incidentally that substitution of the much more polar solvent, acetonitrile, slowed the overall rate to about the same degree as did benzene. From this observation, it is concluded that schemes based on a dipolar intermediate are offered no encouragement and that there is no reason to suspect that the cyano and isopropenyl substituents have fundamentally changed the mechanism from that which operates in cyclopropane or less seriously perturbed derivatives. Appreciable dipolar character was not to be expected in the gas phase in any event.

It remains to investigate the course of the rearrangement at much lower pressures of the order of 10^{-3} mm where, even of molecules of this size, it may be possible to detect a change in the ratio among the three processes as a consequence of small differences in the minimum critical enthalpies and entropies of activation. Given the much longer time needed to explore the less probable paths of lower energies of activation, differences among the three families of reaction may be accentuated. The situation may become more akin to that simulated in theoretical attempts to calculate activation energies, such as that of Salem and his co-workers.[10] Here, the computer is given essentially infinite time to search for the path of lowest energy of activation without regard to the probability of the process and is thus instructed to reject processes of higher activation energy even though their entropies of activation may possibly be more favorable. Between collisions, the molecule itself can be imagined to function as a computer exploring as many combinations of its normal vibrational modes as it has time for. Although it is recognized that activation energy falls off with decreasing pressure as the more slowly reacting, less highly energized molecules make proportionally larger contributions to the overall reaction,[47] it appears not to have been suggested that ratios of products in multipathed unimolecular gas-phase rearrangements may also change as lifetime between collisions is increased.

The relationship of the continuous, nonconcerted pathway hypothesized here to the vinylcyclopropane rearrangement[21] and to thermal reorganizations involving the making and breaking of four-membered rings will be discussed elsewhere. Suffice it to express the caution in respect of certain rearrangements for which energy-lowering, continuously bonded, and, in that sense, concerted processes[23,24] may be hypothesized, that factors such as distance of separation and the as yet unelucidated demands of the rotational component may lead to energetically nonconcerted path-

(47) See reference 36, p 80.

ways of nevertheless striking stereoselectivity owing to the extraordinary efficiency of the self-trapping property of suitably oriented singlet diradicals. Even small activation barriers such as that required to transmute synclinal tetramethylene into its antiperiplanar conformer suffice to convert a continuous, diradical-like, energetically not concerted transition state into an authentic diradical-like intermediate vulnerable to all those observational intrusions which can be effected within its given lifetime.

Experimental Section

General. Optical rotations were determined on a Perkin-Elmer 141 digital readout polarimeter. Nmr spectra were recorded in deuteriochloroform (unless indicated otherwise) on Varian A-60 and T-60 spectrometers and the chemical shifts were reported in ppm downfield from tetramethylsilane. Infrared spectra were determined in carbon tetrachloride (unless stated otherwise) on a Perkin-Elmer Model 337 grating spectrophotometer. Quantitative analyses of mixtures were effected on a Perkin-Elmer Model 990 and a Varian Aerograph A90-P_3 instrument. Relative areas were determined with a Digital Integrator Autolab Model 6300-01. Purification and separation of larger quantities was accomplished by preparative glpc on Aerograph Model A90 and Autoprep Model A-700. The following columns were employed: column A, 10 ft × 0.25 in., 10% GE XE-60, on Chromosorb P; column B, 15 ft × 0.25 in., 10% Carbowax 20M on 50/60 Anakrom ABS; column C, 14 ft × 0.25 in., 10% TCEP (1,2,3-tris(2-cyanoethoxy)propane); column D, 13.5 ft × 0.25 in., 10% Carbowax 20M on 70/80 Anakrom ABS; column E, K-20M (Perkin-Elmer, 300 ft × 0.01 in., capillary column); column F, 12 ft × 0.125 in., 10% Carbowax 20M on 70/80 Anakrom ABS.

Mass spectral analyses were made with an AEI Model MS 9 double focussing mass spectrometer. Microanalyses were carried out by Scandinavian Microanalytical Lab., Herlev, Denmark.

Melting points and boiling points are uncorrected.

Dimethyl trans-Cyclopropane-1,2-dicarboxylate (trans-I). **Method a. Sodium Methoxide in Dimethyl Sulfoxide.** A three-necked, 1-l. flask equipped with mechanical stirrer and condenser was charged with dry DMSO (100 ml), methyl acrylate (Eastman, Technical; 87 g, 1 mol), and methyl chloroacetate (106 g, 1 mol). Sodium methoxide (Fisher; 54 g, 1 mol) was added at 30–40° during 5 hr in a nitrogen atmosphere. Stirring was continued for another 4 hr when 400 ml of water was added. The water-insoluble products were extracted with three 200-ml portions of ether, dried over anhydrous MgSO₄, and distilled to give a fraction (55 g) of bp 56–64° (16 mm) (no cyclopropyl hydrogens in the nmr) and the dimethyl ester of trans-I (65 g; 42%): bp 86° (6 mm); nmr δ 1.4 (complex m, 2 H), 2.18 (complex m, 2 H), 3.7 (s, 6 H).

Method b. Sodium Hydride in Toluene. To a well-stirred suspension of sodium hydride as a 57% dispersion in mineral oil (7.3 g, 0.174 mol) in dry toluene (15 ml) at 60–70°, there was added a mixture of methyl acrylate (14.3 g, 0.166 mol) and methyl chloroacetate (18 g, 0.166 mol) over a 10-min period. An initially slow evolution of hydrogen became vigorous when the bath temperature was raised to 110–115° (internal temperature of 105°). The oil bath had to be removed at times to moderate the reaction. Heating was stopped after 30 min and stirring was continued for another 4 hr. The brown reaction mixture was treated with 1 ml of methanol (to decompose any excess sodium hydride) followed by 20 ml of water to dissolve the inorganic salts. The toluene layer was removed and the aqueous portion was extracted with two 10-ml portions of toluene. The combined organic extracts were washed with two 5-ml portions of water and with brine (5 ml) and dried over MgSO₄. Distillation of the extract afforded the methyl ester of trans-I (16.5 g, 64%), bp 81–83° (6 mm).

When the bath temperature was maintained at or below 100°, a mixture of the dimethyl esters of trans- and cis-I (about 40:60) was obtained in 60% of theory.

Equilibration of Dimethyl Cyclopropane-1,2-dicarboxylate. (a) **With Sodium Methoxide in Dimethyl Sulfoxide.** A mixture (15:85) of the dimethyl esters cf trans- and cis-I (0.5 g, 3.2 mmol) in a 25-ml, round-bottom flask with side arm closed with a serum cap was treated with dry DMSO (1.5 ml) and sodium methoxide (Eastman, 70 mg, 1.3 mmol) added portionwise under an atmosphere of nitrogen. The mixture turned yellowish brown and was stirred for 30 min at 25°. Thereupon 5 ml of water was added, extraction with

two 15-ml portions of ether was effected, and the combined extracts were washed with water, dried over MgSO₄, and concentrated by distillation. The nmr spectrum of the residue was essentially identical with that of pure dimethyl ester of *trans*-I.

(b) With Sodium Hydride in Toluene. A mixture of the dimethyl esters of *cis*- and *trans*-I (1.6 g, 10.1 mmol) in 5 ml of toluene containing 0.13 g of 57% dispersion of NaH (3.08 mmol) was heated at a bath temperature of 90–120° for 4.5 hr. The brown reaction mixture was cooled to room temperature and diluted with 5 ml of water. The toluene solution was removed, combined with a toluene extract (20 ml) of the aqueous portion, washed with water, and dried over MgSO₄. Distillation afforded a residue (1.2 g, 75%), the nmr spectrum of which was that of dimethyl ester of *trans*-I.

trans-**Cyclopropane-1,2-dicarboxylic Acid** (*trans*-I). A mixture of sodium hydroxide (98 g) in water (520 ml) and dimethyl *trans*-cyclopropane-1,2-dicarboxylate (130 g, 0.82 mol) was heated under reflux for 8 hr, cooled in an ice bath, and partially neutralized (~pH 7) with concentrated aqueous HCl. After removal of alcohol by distillation (at 16 mm), the remaining solution was cooled in an ice bath and acidified with concentrated aqueous HCl. Seven extractions with 150-ml portions each of ether were combined, dried, and concentrated to give 92 g (86% of theory) of colorless crystalline cyclopropane-1,2-dicarboxylic acid (*trans*-I): mp 175–176.5° (lit.[13] mp 176–177°); nmr (D₂O) δ 1.42 (complex m, 2 H) and 2.18 (complex m, 2 H).

Resolution of *trans*-**Cyclopropane-1,2-dicarboxylic Acid** (*trans*-I). **(a) Brucine.** A partial resolution has been reported.[15] *trans*-I (3.9 g, 30 mmol) in 100 ml of water was added to a solution of brucine (23.64 g, 60 mmol) in 100 ml of 95% ethanol, diluted with 110 ml of water, and stored for 5 hr at room temperature. As no solid separated during this period, most of the ethanol was removed under vacuum leaving an aqueous solution from which 14.5 g of colorless crystals, [α]²⁷₅₇₈ −27° (c 0.868, EtOH), deposited on standing at room temperature overnight. Five recrystallizations from water gave 3.4 g of brucine salt, [α]²⁷₅₇₈ +1° (c 0.830, EtOH), which was hydrolyzed with 10% aqueous NaOH, brucine was removed by filtration, and the aqueous solution was extracted with 20 ml of methylene chloride. The aqueous solution was then acidified with cold 10% dilute HCl, continuously extracted with ether for 12 hr, and the dried ethereal extract was concentrated to give 0.28 g of (+)-*trans*-I: mp 171–172.5°; [α]²⁷D +218° (c 0.161, EtOH) [lit. [α]D +84.5°[15] (c 2.02, H₂O), 227°[16] (c 2.34, EtOH)]. Crystallization of the diacid from ethyl acetate–petroleum ether did not change the rotation significantly.

(b) Quinine, One Equivalent. A solution of *trans*-I (53.8 g, 0.414 mol) and quinine (134 g, 0.414 mol) in 1:3 ethanol–ethyl acetate (1400 ml) was stored at 5° for 3 days to yield 37 g of crystalline salt. A sample of *trans*-I, recovered from 0.55 g of this salt by suspension in water, acidification with cold 20% HCl, extraction six times with 20-ml portions of ether, and concentration to a residue of 75 mg, had [α]²⁷₅₇₈ −188° (c 0.5825, EtOH). The mother liquor on keeping at 5° for an additional 48 hr yielded a second crop of crystals (38 g) from which diacid, [α]²⁷₅₇₈ +127° (c 0.837, EtOH), was obtained. The filtrate when stored at 20° for 30 hr deposited a third crop (30 g); diacid: [α]²⁷₅₇₈ −208° (c 0.555, EtOH). Two recrystallizations of the first and the third crops furnished a total of 45 g of salt which gave 6 g of (−)-*trans*-I, [α]²⁷₅₇₈ −230.2° (c 0.470, EtOH). A sample of this salt, crystallized from absolute MeOH and dried at 110° (0.05 mm) for 48 hr, had mp 160–163°. *Anal.* Calcd for C₄₃H₅₄N₆O₈: C, 69.4; H, 7.0; N, 7.2. Found: C, 69.0; H, 7.0; N, 7.3.

(c) Quinine, Two Equivalents, from Ethyl Acetate–Ethanol. *trans*-I (2.6 g, 20 mmol) and quinine (13.96 g, 40 mmol) were dissolved in 50 ml of absolute ethanol, diluted with 150 ml of ethyl acetate, and kept at room temperature for 3 hr, whereupon a colorless solid had crystallized (6 g). A portion was converted to *trans*-I, [α]²⁷₅₇₈ −166.4°. The remainder of the salt was crystallized twice from ethanol–ethyl acetate (3:5) to give material of mp 145–147° from which *trans*-I, [α]²⁷₅₇₈ −231.5° (c 0.326, EtOH), was obtained.

(d) Quinine, One Equivalent, from Ethanol–Water. *trans*-I (3.9 g, 30 mmol) in 15 ml of water was added to a solution of quinine (9.72 g, 30 mmol) in 30 ml of ethanol and freed of most of the ethanol by distillation. The residue was then crystallized from 60 ml of water–ethanol (4:1) at room temperature. Recrystallization from the same solvent followed by a second recrystallization from absolute ethanol gave 0.55 g of needle-like crystals, mp 170–172°; [α]²⁷₅₇₈ −135.7° (c 0.696, EtOH). Fractional crystallization of the filtrates from water–ethanol (4:1) gave another 1.7 g of material, mp 170–172°, [α]²⁷₅₇₈ −137.1° (c 0.554, EtOH); regenerated *trans*-I

(0.43 g from the combined samples) had [α]²⁷₅₇₈ +198.7°, [α]²⁷₅₈₉ +188.5° (c 0.382, EtOH).

Dimethyl (−)-*trans*-**Cyclopropane-1,2-dicarboxylate** (**Dimethyl Ester of** (−)-*trans*-I). Treatment of (−)-*trans*-I, [α]²⁷₅₇₈ −231.6° (c 0.541, EtOH), with ethereal diazomethane at 0° afforded dimethyl ester which, when distilled at 72° (6 mm) (97% of theory), solidified immediately: mp 34.5–35°; [α]²⁷₅₇₈ −231.9° (c 0.442, MeOH); nmr δ 1.4 (complex m, 2 H), 2.18 (complex m, 2 H), 3.7 (s, 6 H).

(−)-*trans*-**2-Carbomethoxycyclopropyldimethylcarbinol.** **(a) Inverse Addition.** In a 250-ml, three-necked flask equipped with reflux condenser, magnetic stirrer, and dropping funnel, methylmagnesium bromide was prepared from 3.43 g (0.143 mol, 10% excess) of magnesium metal and 13.9 g (8 ml, excess) of methyl bromide in 140 ml of ether. The resulting solution was cooled to room temperature and added dropwise within 1.5 hr to a stirred solution of 10.02 g (0.063 mol) of dimethyl ester (−)-*trans*-I, [α]²⁷₅₇₈ −231.1° (c 0.6088, EtOH), in 160 ml of anhydrous ether at −3 to 0°. After the addition, the reaction mixture was stirred for 6 hr at room temperature and hydrolyzed with saturated NH₄Cl solution. The precipitated salts were removed by filtration and washed thoroughly with ether. The ether filtrate was dried over MgSO₄ and concentrated by distillation to give 9.3 g of product consisting of the carbinol (95%) and unreacted ester (5%). Analysis was by glpc on column A at 125°, the retention times being 11 and 7 min, respectively.

A small amount of pure carbinol was separated by preparative gas chromatography on column A: [α]²⁷₅₇₈ −100°, [α]D −94.6° (c 0.459, EtOH); nmr δ 0.89–1.2 (complex m, 2 H), 1.23 (s, 6 H), 1.62 (complex m, 2 H), 2.5 (broad s, 1 H), 2.68 (s, 3 H); ir (cm⁻¹) 3620 w, 3500 w (OH), 2920 m (CH), and 1735 s (C=O).

(b) Normal Addition and Four Equivalents. A solution of 3.16 g (20 mmol) of dimethyl ester (±)-*trans*-I in ether (50 ml) was added dropwise with stirring to a solution of methylmagnesium bromide prepared from 2.14 g (89 mmol, 10% excess) of magnesium metal. The reaction mixture was heated under reflux for 4 hr and stirred overnight (12 hr) at room temperature. An isolation procedure similar to that described for (−)-*trans*-2-carbomethoxycyclopropyldimethylcarbinol furnished 3.1 g (98%) of a colorless solid. It was recrystallized from ether–petroleum ether (1:1) to give colorless crystals of the bis tertiary alcohol: mp 63–64°; nmr δ 2.45 (s, 2 H) 1.23 (s, 6 H), 1.15 (s, 6 H), 0.9 (m, 2 H), 0.4 (m, 2 H). *Anal.* Calcd for C₉H₁₂O₂: C, 68.3; H, 11.5. Found: C, 68.4; H, 11.4.

Methyl (−)-*trans*-**1-Isopropenylcyclopropane-2-carboxylate** (**II**). The 95:5 mixture of the tertiary carbinol and dimethyl ester of *trans*-I was treated with a trace of concentrated H₂SO₄, and heated to 70–80° under reduced pressure to remove the product as formed by distillation (bp 45° (2.5–3 mm)). An ethereal solution of the distillate was washed with cold water, dried over MgSO₄, and concentrated to give a colorless liquid (70% yield). Glpc analysis on column B at 135° revealed one major peak with retention time 14 min and three minor peaks (about 5% combined) with retention times of 25, 42, and 98 min. The main product was collected by preparative gas chromatography using the same column: [α]²⁷₅₇₈ −221.6°, [α]²⁷D −211.6° (c 0.5955, MeOH); nmr δ 1.67 (s, 3 H), 3.73 (s, 3 H), 4.81 (s, 2 H), and 0.9–2.2 (complex m, 4 H); ir (cm⁻¹) 1735 s (C=O), 1170 s (C—O—C), and 885 m (C=CH₂); mass spectrum m/e 140 (calcd for C₈H₁₂O₂, 140). *Anal.* Calcd for C₈H₁₂O₂: C, 68.4; H, 8.6. Found: C, 68.7; H, 8.7.

Thermal Rearrangement of (−)-*trans*-**II.** A sample of (−)-*trans*-II [0.49 g, [α]²⁷D −211.6° (c 0.5955, MeOH)] was placed in a Pyrex ampoule (3.5 cm i.d., 56 cm long) along with 25 mg of recrystallized diphenylamine. The sample was degassed and sealed under reduced pressure (10⁻⁴ mm), and heated in a tube furnace at 280°. Temperature was measured periodically with a thermocouple placed at the middle of the tube. Recovered product was analyzed on column C at 125°. The two peaks consisted of a major component identified as starting material by retention time and its nmr and ir spectra and a minor component which was rechromatographed twice on the same column to ensure complete removal of *trans*-II and was then resolved on column B at 110° into two components with retention times of 32 and 38 min. These were separated by preparative glpc using the same column (B) and were identified as *cis*-II and -III, respectively, by the comparison of their nmr and ir spectra with those of authentic materials (*cis*-II described below; III to be reported later[21]). The results of one illustrative experiment are given in Figure 2.

Ethyl *cis*-**2-Isopropenylcyclopropane-1-carboxylate** [*cis*-II (Ethyl Ester)]. A mixture of freshly distilled isoprene (80 ml) and ethyl diazoacetate (40 g) was irradiated with a 275-W General Electric RS

sunlamp in a 250-ml round-bottom Pyrex flask equipped with an efficient reflux condenser and a nitrogen bubbler and cooled externally with tap water. After 48 hr, the excess isoprene was distilled at atmospheric pressure and the remaining mixture was fractionated in a 14-cm Vigreux column. Unreacted ethyl diazoacetate distilled first, followed by the product (7 g), bp 50–53° (1.5 mm). Analysis by means of glpc column C at 120° revealed four peaks with retention times of 25, 28, 35, and 42 min in the ratio 12:17:43:28, respectively. Isolation of pure components was effected with the same column. The two peaks with retention time 35 and 42 min were identified by nmr as ethyl *trans*-2-isopropenyl-cyclopropane-1-carboxylate and ethyl *cis*-2-isopropenylcyclopropane-1-carboxylate, respectively. The important difference in the nmr spectrum of *cis*-II (ethyl ester) and *trans*-II (ethyl ester) involves the olefinic protons which appear as two unresolved multiplets at δ 4.84 and 4.95 in the former and essentially as a single peak at δ 4.77 in the latter.

Thermal Rearrangement of *cis*-II (Ethyl Ester). A sample of *cis*-II (ethyl ester) was degassed, sealed in a Pyrex ampoule under reduced pressure, and heated in a furnace at 282° for 6 hr. Analysis by glpc column C at 125° revealed three peaks with retention times 37, 42, and 44 min in the ratio 62:29:9, respectively. The first two peaks were collected and identified by their nmr spectra as *trans*-II (ethyl ester) and III (ethyl ester), respectively. There was too little of the third substance for isolation, which was assumed to be starting material from its retention time.

cis-2-Isopropenylcyclopropane-1-carboxylic Acid [*cis*-II (Acid)]. A sample of *cis*-II (ethyl ester) (0.65 g as synthesized above) was saponified with 9 ml of 3.3% KOH in 66% aqueous EtOH at 85–90° for 10 hr. After removal of ethanol under reduced pressure, the residue was cooled in ice, diluted with 1 ml of water, acidified with ice-cold 4 N HCl, and extracted with three 30-ml portions of ether. The combined extracts were washed with water, dried over MgSO₄, and concentrated by distillation to give 0.53 g (99% of theory) of *cis*-II (acid): mp 48–49°; nmr δ 1.75 (s, 3 H), 0.9–2.1 (broad m, 4 H), 4.86 and 4.96 (two overlapping m, 2 H), and 10.95 (s, 1 H).

Resolution of *cis*-II (Acid) with Ephedrine. A solution of *cis*-II (acid) (0.63 g) in ethyl acetate (2 ml) combined with a solution of ephedrine (0.83 g) in ethyl acetate (3 ml) was diluted with 15 ml of petroleum ether (45–60°). On keeping 16 hr at room temperature 0.3 g of the salt crystallized: mp 85–92°, $[\alpha]^{27}{}_{578}$ −46.5° (c 0.560, MeOH). A first recrystallization from 8 ml of ethyl acetate–petroleum ether (1:2) for 8 hr at 5° gave 0.2 g of salt, $[\alpha]^{27}{}_{578}$ −55.4° (c 0.470, MeOH); a second recrystallization gave 0.13 g, $[\alpha]^{27}{}_{578}$ −60.8 (c 0.360, MeOH). Fractional crystallization of the filtrates furnished an additional 65 mg of salt of this purity. The two samples were combined; acid was regenerated by acidifying with cold dilute HCl and extracting with ether. The extracts were treated with ethereal diazomethane, dried over MgSO₄, and concentrated by distillation to a residue which was isolated pure (80 mg) by preparative glpc (column C at 125°): $[\alpha]^{27}{}_{578}$ −14.6°, $[\alpha]_{365}$ −59.4° (c 0.281 MeOH); nmr spectrum identical with that of (−)-*cis*-II obtained from the rearrangement of (−)-*trans*-II.

Thermal Rearrangement of (−)-*cis*-II. Methyl (−)-*cis*-2-isopropenylcyclopropane-1-carboxylate (70 mg, $[\alpha]^{27}{}_{578}$ −14.6°) and 5 mg of recrystallized diphenylamine was degassed, sealed in a Pyrex ampoule under reduced pressure (10^{-4} mm), and heated in a furnace at 280 ± 10° for 4 hr. Glpc on column C at 125° yielded two products with retention times of 34 and 39 min in the ratio 76:24, respectively. The first substance had the same ir and nmr spectra as that of *trans*-II and $[\alpha]^{27}{}_{578}$ −3.1° (c 1.05, MeOH). The second peak was a mixture further resolved by glpc on column B at 105° into two peaks in the ratio 25:75. The first had the same retention time as that of *cis*-II (30 min) but was present in too small an amount for further confirmation of identity and had retained about 2% of its initial optical activity, while the second material (retention time 34 min) had an ir spectrum identical with that of synthetic methyl 1-methylcyclopentene-4-carboxylate[21] (III): $[\alpha]^{27}{}_{365}$ +5.7°, $[\alpha]^{27}{}_{578}$ +1° (c 0.660, MeOH).

(−)-*trans*-2-Isopropenylcyclopropane-1-carboxamide. (a) From (−)-*trans*-II (Acid). Saponification of the total product of dehydration [(−)-*trans*-II; $[\alpha]_{578}$ −221.6°] with ethanolic KOH according to the procedure described above for *cis*-II (ethyl ester) afforded (−)-*trans*-II as the carboxylic acid.

A solution of 1.58 g (12.5 mmol) of the above product in 15 ml of CH₂Cl₂ (distilled over P₂O₅) and 1.74 ml (12.5 mmol) of triethylamine was added dropwise with stirring to a solution of 1.18 ml (12.5 mmol) of ethyl chloroformate in 10 ml of CH₂Cl₂ cooled to −25° during a 20-min period. After the mixture had been stirred for 1.5 hr at −20 to −5°, NH₃ was bubbled through

for 15 min. After a 1.5-hr period of further stirring at 25°, the solid material was filtered and washed twice with CH₂Cl₂. The combined CH₂Cl₂ solutions were washed with water, dried over MgSO₄, and concentrated under reduced pressure to give 1.25 g of colorless solid. A sample, after two recrystallizations from CH₂Cl₂–petroleum ether gave colorless needles: mp 109–110°; $[\alpha]^{27}$D −203.6° (c 0.360, EtOH), nmr δ 6.44 (broad s, 2 H), 4.8 (unresolved m, 2 H), 1.7 (unresolved m, 3 H), and 0.83–2.3 (broad m, 4 H); ir (cm⁻¹) 1675 (C═O) and 890 (C═CH₂).

A sample of the racemic amide after recrystallization from CH₂-Cl₂–petroleum ether gave colorless needles, mp 146–148°.

(b) From (−)-*trans*-II. To a solution of (−)-*trans*-II (0.9 g), $[\alpha]_{578}$ −222° (c 0.5955, MeOH), after purification on column B at 135°, in THF (5 ml), 30% NH₄OH (20 ml) was added and the heterogeneous mixture was stirred overnight. An additional quantity of 15 ml of NH₄OH and 5 ml of MeOH was added and the mixture was stirred for another 25 hr. Removal of solvents in a rotary evaporator gave 0.6 g of colorless solid which was crystallized from CH₂Cl₂–petroleum ether at 15°: colorless needles; mp 109–110°; $[\alpha]^{27}$D −202.9° (c 0.5076, EtOH). *Anal.* Calcd for C₇H₁₁NO: C, 67.2; H, 8.9; N, 11.2. Found: C, 66.9; H, 8.9; N, 11.1.

trans-1-Cyano-2-isopropenylcyclopropane (*trans*-IV). A 25-ml three-necked flask fitted with a three-way stopcock and a serum cap was charged with 1.2 g (9.5 mmol) of the crude carboxamide while a slow stream of dry nitrogen was passed through the stopcock. Dry pyridine (1.5 ml) was introduced through the serum cap with a syringe. To the resulting suspension cooled to 5°, 1.8 g (9.5 mmol) of *p*-toluenesulfonyl chloride[48] in 2 ml of pyridine was added with stirring over a period of 20 min at 2–5°. After having stirred for 8 hr at 10 to 22°, the mixture was treated with anhydrous ether (50 ml), stirred for 5 min, freed of precipitated material by filtration, and washed with two 10-ml portions of ether. The combined ethereal solution was washed with ice-cold 0.1 N HCl until the aqueous extract was weakly acidic. The ether extract was dried over MgSO₄ and concentrated by distillation to a product which after purification by preparative glpc on column D at 145° afforded 0.55 g of colorless liquid: $[\alpha]^{27}{}_{578}$ −212.6°, $[\alpha]_{589}$ −203.4° (c 0.4888, Spectrograde cyclohexane); nmr (CCl₄) δ 4.77 (unresolved m, 2 H), 1.7 (unresolved m, 3 H), 1.67–2.2 (m, 1 H), 1.0–1.43 (m, 3 H); ir (cm⁻¹) 2240 m (C≡N) and 892 m (C═CH₂). Anal. Calcd for C₇H₉N: C, 78.5; H, 8.5; N, 13.1. Found: C, 78.0; H, 8.2; N, 13.2.

cis-1-Cyano-2-isopropenylcyclopropane (*cis*-IV). To (−)-*trans*-IV (0.38 g), $[\alpha]^{28}{}_{578}$ −204°, $[\alpha]$D −196° (c 0.429, Spectrograde cyclohexane), in a 10-ml flask with a side arm closed with a serum cap and swept with dry N₂, 2.5 ml of DMSO (stored over Linde molecular sieves, Type 4A) was introduced with a syringe. To the resulting solution, cooled to 15° in an ice bath, about 30 mg of freshly sublimed potassium *tert*-butylate was added in portions. After being stirred for 5 min at 15°, the mixture was diluted with 5 ml of cold water and extracted with three 30-ml portions of *n*-pentane. The pentane extract was washed with water, dried over MgSO₄, and concentrated to an oil which was analyzed by glpc on capillary column E at 130° into two peaks corresponding to *trans*-IV and *cis*-IV in the ratio 64.8:35.2. In a similar experiment starting with (+)-*cis*-IV, a ratio of 63.4:36.6 was obtained. For measurement of specific rotation, the two substances were separated on column D and the *cis*-IV obtained was rechromatographed to remove traces of *trans*-IV: recovered *trans*-IV had $[\alpha]^{27}{}_{578}$ −205.9°, $[\alpha]^{27}$D −196° (c 0.4005, Spectrograde cyclohexane). *Anal.* Calcd for C₇H₉N: C, 78.5; H, 8.5; N, 13.1. Found: C, 77.9; H, 8.5; N, 13.2.

In a separate experiment, 40 mg of (−)-*trans*-IV, $[\alpha]^{27}{}_{578}$ −126.2°, in 0.25 ml DMSO was treated with 5 mg of potassium *tert*-butylate and the mixture was stirred for 30 min at 25°. The product mixture was recovered and separated as described above: recovered *trans*-IV had $[\alpha]^{27}{}_{578}$ −126.4°.

Thermal Rearrangement of *trans*-IV. Isolation of 1-Methyl-4-cyanocyclopentene (V). *trans*-IV (75 mg) was degassed and transferred *in vacuo* into an ampoule of Corning 0120 glass, 56 × 3.5 cm with a 15 × 0.6 cm tubing at the open end; the ampoule was sealed under reduced pressure (10^{-4} mm), heated in a furnace at 262 ± 3° for 18 hr, and cooled to room temperature. The tip of the narrow end was cooled in liquid N₂ to collect the product and broken off. Analysis of the total product by glpc on column B at 130° gave three peaks with retention times 29, 34, and 44 min in the

(48) T. Itoh, *Bull. Chem. Soc. Jap.*, **36**, 25 (1963).

ratio 17:78:6. The major peak was separated and identified as 1-methyl-4-cyanocyclopentene: nmr δ 5.27 (m, 1 H); 1.74 (unresolved m, 3 H); 2.43–3.37 (m, 5 H); ir (cm⁻¹) 2230 (C≡N). The minor components with retention times 29 and 44 min corresponded to recovered *trans*-IV and *cis*-IV, respectively.

Kinetics of Rearrangement of *cis*-IV and *trans*-IV. (a) General. Thermal rearrangements in the gas phase were effected in sealed Pyrex ampoules suspended in the vapors of boiling naphthalene (217.8°). Recrystallized naphthalene was maintained at a gentle reflux in a 1-l. Pyrex flask with a 46 × 5-cm neck, the lower 36 cm of which was insulated with several layers of asbestos and a final wrapping of Fiberglas. The uncovered upper portion of the column served as an air-cooled condenser. The temperature of the vapors was measured with an iron–constantan thermocouple and a Leeds and Northrup No. 8686 millivolt potentiometer. No significant temperature gradient was noted across the lower 25-cm section of the insulated neck. In no runs did the temperature fluctuate more than ±0.3° and in most only ±0.1°.

Before use, samples of *cis*-IV and *trans*-IV were purified by preparative glpc on column D, subjected to one vacuum transfer, degassed, and transferred by micro syringe into the ampoules which were degassed at least twice and sealed under reduced pressure (10⁻⁴ mm). The ampoules were suspended by means of a fine copper wire fastened to a hook at the sealed end. The time lag between the insertion of ampoules and the attainment of ultimate temperature of the vapors above the ampoules was less than 1 min. The ampoules were removed at predetermined time intervals, cooled and their tips were placed in liquid nitrogen to collect the products.

Per cent conversion to the corresponding diastereoisomer was determined in neglect of cyclopentene V (which was less than 1% starting from *trans*-IV and not more than 2% starting from *cis*-IV over the range investigated) by glpc analyses of the products on column E at 130° for each run. Separation into chromatographically pure components was effected by preparative glpc on column D at 140°. Optical rotations were measured at five different wavelengths on samples of *trans*-IV obtained either directly in thermal isomerizations or indirectly by equilibration of the samples of *cis*-IV.

(b) Geometric Isomerization. Samples (2 mg) of racemic *trans*-IV and *cis*-IV along with benzonitrile were heated in sealed Pyrex ampoules 8 × 0.7 cm. Results of glpc analysis of the product mixtures at each point are given in Tables II and III. Two additional kinetic runs (2 and 3) were carried out without the internal standard and the data are collected in Table VII.

Table VII. Kinetic Data for Geometric Isomerization of *trans*-IV and *cis*-IV (Runs 2 and 3)

Run	Time, min	Starting material, *trans*-IV; product, *cis*-IV, %	Starting material, *cis*-IV; product, *trans*-IV, %
2ᵃ	46.0	2.38	7.28
	90.0	4.56	12.91
	150.0	7.30	20.41
	220.0	9.93	27.35
	434.0		44.35
3ᵇ	46.5	2.62	8.21
	90.0	5.26	14.20
	150.0	8.56	21.29
	220.0	10.37	29.76
	310.0	13.54	

ᵃ Glpc analyses of the product were effected on column E using Digital Integrator. The values (±0.02) are means of three analyses at each point. In this run no internal standard was used. ᵇ Glpc analyses of the products effected on column F at 138°. Relative areas were determined by cutting and weighing the recorder tracings. The values (±0.5) are means of three analyses at each point.

The rate constants for the reaction

$$\textit{cis}\text{-IV (B)} \underset{k_{t,c}}{\overset{k_{c,t}}{\rightleftharpoons}} \textit{trans}\text{-IV (A)}$$
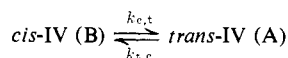
and its reverse were obtained by the usual equation for reversible first-order reactions: $-\log x = -\log[(AK - B)/(A_0K - B_0)] =$

$t(k_{t,c} + k_{c,t})/\ln 10$ where B_0 and B are the concentrations of *cis*-IV at times, zero and t (in seconds), respectively, and A refers to *trans*-IV. The data in Tables II, III, and VII were analyzed by a least-squares computer program where $K = k_{t,c}/k_{c,t}$ was varied by trial and error until a value was found which gave identical values of $(k_{t,c} + k_{c,t})$ starting with either *cis*-IV or *trans*-IV. From the data for run 1 which is plotted in Figure 5, starting from *trans*-IV, $-\log x = (0.00065 \pm 0.000483) + (37.342 \pm 0.098 \times 10⁻⁶)t$, while from *cis*-IV, $-\log x = (-0.00144 \pm 0.00129) + (37.332 \pm 0.262 \times 10⁻⁶)t$, when $K = [\text{cis}]/[\text{trans}] = 26.73/73.27 = 0.3648$. The rate constants for geometric isomerization obtained in runs 1, 2, and 3 are given in Table IV.

(c) Kinetics of Optical Isomerization of (−)-*Trans*-IV. (i) Racemization of (−)-*trans*-IV. In a typical run, 0.48 g of *trans*-IV, $[\alpha]^{27}$D −203.4°, was distributed equally in ten ampoules, 20.3 × 1.25 cm with a 5.0 × 0.6 cm tubing at one end. The sealed ampoules were heated for 46.5 min at 217.8° and the product from all the ampoules was combined to give 0.475 g of colorless liquid which was separated by preparative glpc into *trans*-IV (0.411 g), $[\alpha]^{27}$D −196°, and *cis*-IV (14 mg). Analysis at each point gave the results reported in Table II. Not shown are results obtained at 578, 546, and 436 nm. For the observed log α_0/α vs. t(min), see Figure 6. The data were fitted to a straight line by the method of least squares: log $(\alpha_0/\alpha) = (-0.00438 \pm 0.00097) + (4.253 \pm 0.051 \times 10⁻⁴)t$, whence by multiplication by ln 10 and division by 60, $(k_\alpha)_T = 16.32 \pm 0.20 \times 10⁻⁶$ sec⁻¹.

(ii) Optical Purity of the Product *cis*-IV. The sample of *cis*-IV obtained above was rechromatographed twice to remove traces of *trans*-IV when 11 mg of chromatographically pure (glpc on column E) sample of *cis*-IV was recovered. This was equilibrated by the usual procedure and the mixture of *cis*-IV and *trans*-IV was separated on column D: *trans*-IV had $[\alpha]$D −71.32°. Results of analysis at each point are reported in Table II. Slope and intercept of the observed $[\alpha]$D vs. time (Figure 7) was calculated by the least-squares treatment of the data in Table II. The intercept gave the

$$m = (-8.92208 \pm 0.30347) \times 10⁻⁴ \text{ sec}⁻¹$$

$$\text{intercept } a = -74.05 \pm 0.343°$$

optical purity of the product of rearrangement hence the enantiomeric distribution at zero time defined as R_A (see Figure 8).

(d) Kinetics of Optical Isomerization of (+)-*cis*-IV. (i) Racemization of (+)-*cis*-IV. In a typical run 40 mg of *cis*-IV, $[\alpha]^{27}$D +3.9° (corresponding *trans*-IV had $[\alpha]^{27}$D − 179.2°), was heated in a sealed Pyrex ampoule (same size as for *trans*-IV above) for 46 min at 217.8°. The product was separated on column D; the recovered *cis*-IV (30 mg) was rechromatographed twice and equilibrated by the usual procedure. The mixture of *trans*-IV and *cis*-IV was separated on the same column (D), the *trans*-IV had $[\alpha]^{27}$D −171.3°. Similar procedure for the analysis of all other points gave the results shown in Table III. A plot of log (α_0/α) against time afforded, by the method of least squares, the equation for the straight line, log $(\alpha_0/\alpha) = (-0.00718 \pm 0.00423) + (5.649 \pm 0.296 \times 10⁻⁴)t$ whence $(k_\alpha)_C = 21.68 \pm 1.13 \times 10⁻⁶$ sec⁻¹.

(ii) Optical Purity of the Product *trans*-IV. The sample of *trans*-IV obtained had $[\alpha]^{27}$D −63.5°. The results for all the points are given in Table III. Slope and intercept of the observed $[\alpha]$D vs. time (min) plot (Figure 7) were calculated by least-squares treatment of the data in Table III. The intercept which is the specific rotation

$$m = (-9.3036 \pm 0.1791) \times 10⁻⁴ \text{ sec}⁻¹$$

$$\text{intercept } a = -66.03 \pm 0.153°$$

of the product at zero time, gave the ratio of the enantiomers defined as R_A (see Figure 8).

Thermal Isomerization at Low Pressure and in Solution. To determine the effect of pressure, the isomerization of (−)-*trans*-IV and of (+)-*cis*-IV was carried out at 1–2 mm pressure in a 12-l. Pyrex flask heated in an air thermostat at 217.5°.²⁵ᵇ No change in the racemization of the starting material or in the retention of optical purity of the product was observed. The rearrangement was also studied in benzene and in acetonitrile solutions at 217.8°. The rate of racemization and geometrical isomerization decreased in going from lower to higher pressure while the retention of optical purity in the diastereomeric products remained unchanged. The results of these experiments are summarized in Table V.

(a) Thermal Isomerization of (−)-*trans*-IV. (i) At 2 mm Pressure. Rearrangement was carried out in a 12-l. Pyrex flask heated in an air-thermostat at 217°. (−)-*trans*-IV (100 mg), $[\alpha]$D −165.5°

(81.4% optical purity based on maximum [α]D −203.4°), was vacuum transferred within 5 min. After 310 min, the product was withdrawn quantitatively into a receiver cooled in liquid nitrogen. Analysis and separation of the product mixture were performed as described earlier. The recovered starting material *trans*-IV had [α]D −119.7° (c 0.3816, Spectrograde cyclohexane) which corresponds to 72.3% retention of optical purity. The optical purity of the *cis*-IV was determined as usual *via* conversion to *trans*-IV, [α]D −47.4°.

(ii) **In Acetonitrile.** A solution of (−)-*trans*-IV (20 mg), [α]D −151.5° (74.5% optical purity), in Spectrograde acetonitrile (0.3 ml) was heated in a thick-walled sealed Pyrex ampoule 0.8 cm i.d., 15.2 cm long at 217.8° for 220 min. The recovered (−)-*trans*-IV had [α]²⁸D −130.6° (86.2% retention of optical activity). The amount of *cis*-IV formed was 9.9%.

(b) **Thermal Isomerization of (+)-*cis*-IV.** (i) **At 1 mm Pressure.** (+)-*cis*-IV (50 mg), obtained by the base-catalyzed epimerization of (−)-*trans*-IV, [α]D −196° (96.3% optical purity), was vacuum transferred within 5 min into the 12-l. flask (see above) and

heated for 150 min at 217.5°. The product was recovered almost quantitatively. It was analyzed and separated as described earlier. The optical purity of the recovered *cis*-IV was determined as usual *via* *trans*-IV, [α]D −161.8° (82.5% retention of optical activity). The product *trans*-IV had [α]D −63.7°.

(ii) **In Benzene.** A solution of (+)-*cis*-IV (30 mg) of 96.3% optical purity, in 0.5 ml of dry benzene, was heated in a thick-walled sealed Pyrex ampoule 0.8 cm i.d., 15.2 cm long for 150 min at 217.8°. The optical activity of the recovered *cis*-IV was determined through its conversion to *trans*-IV, [α]D −175° (89.3% retention of optical activity). The product *trans*-IV had [α]D −62°.

1,1'-Azobisformamide. I. Photochemical Decomposition in Solution[1]

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Abstract: The photolysis of 1,1'-azobisformamide (ABFA) has been investigated in DMSO solution (λ >300 nm). The major photolysis products are N_2 (0.98–1.0 mol/mol of ABFA), CO (0.87–0.97) and urea (0.78). Ammonia and biuret are minor products (*ca.* 0.04–0.07). The photolysis is characterized by an induction period preceding the appearance of decomposition products. Spectrophotometric experiments indicate that the isomerization of ABFA is the only photochemical process occurring. Evidence is presented for a decomposition mechanism involving the cyclization of *cis*-ABFA to 1,2,4-triazoline-3,5-dione followed by thermal decomposition (25°) of the latter. The photolysis of *N,N'*-diethylazobisformamide under the same conditions yields primarily 4-ethylurazole while *N,N,N',N'*-tetramethylazobisformamide yields its cis isomer as the only photolysis product.

The thermal decomposition of α,α'-dicarbonyl azo compounds has not received a great deal of study, although their use as dienophiles[2] and as oxidants[3] has been investigated extensively. Published work on the thermal decomposition[4] suggests that free radicals are intermediates, analogous to the recognized behavior of aliphatic azo compounds. Photolysis, on the other hand, may involve several processes. For example, both photoisomerization[5] and homolytic pathways[4i] are important for azodicarboxylates. The mechanism of

photodecomposition of dimethyl azodicarboxylate has been considered only briefly, with the conclusion that free radicals are intermediates.[4a] Photolysis of dibenzoyldiimide[4e] and both *o,o'*- and *p,p'*-dichloro derivatives[6] yields predominantly benzils by a process that may involve isomerization to cis followed by simultaneous loss of nitrogen and formation of the carbon–carbon bond.[4f] Of all the α,α'-dicarbonyl azo compounds investigated, azobisformamides are among the least studied. Our primary interest is in the parent compound 1,1'-azobisformamide (ABFA). This compound possesses considerable thermal stability. In the solid state it does not decompose significantly at temperatures below 190°. It is insoluble in most common solvents and possesses only limited solubility in dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and similar solvents. Its decomposition mechanism in solution has never been reported. We have undertaken an investigation of its decomposition and are reporting herein the results of a study of its photolysis in solution.

$$H_2NCON{=}NCONH_2$$
ABFA

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