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The Continuous Diradical as Transition State. II. Internal Rotational Preference in the Cyclopentene Rearrangement of the Vinylcyclopropanes, (1*S*,2*R*)-(+)-*cis*- and (1*R*,2*R*)-(−)-*trans*-1-Cyano-2-isopropenylcyclopropane

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Abstract: Stereochemical dissection of the 4-cyano-1-methylcyclopentene obtained from thermal rearrangement of *cis*- and *trans*-1-cyano-2-isopropenylcyclopropane has revealed partial retention of optical activity (a freely rotating diradical as intermediate requires racemic product) owing to predominance of retention of configuration from cis and of inversion of configuration from trans (some factor(s) beyond control by orbital symmetry become important). Pending quadrisection of the rearrangement, a tentative description in terms of a not-obviously-concerted reaction involving rotational preference within the framework of the continuous diradical hypothesis is offered.

Study of an optically active vinylcyclopropane was undertaken to elucidate the chiral and configurational characteristics of a not obviously concerted thermal rearrangement. The first phase, which dealt with the enantiomerization and diastereomerization of the cyclopropane ring,[1] is now extended to include the ring enlargement to cyclopentene.[2]

The large enthalpy change in the vinylcyclopropane rearrangement ($\Delta H \sim -22$ kcal/mol)[5] generally makes the rearrangement irreversible, except in those instances in which strain in the cyclopentene matches exothermicity[3] or exceeds it.[8]

The experimental enthalpy of activation ($\Delta H^{\ddagger}$ 48.5 kcal/mol)[9] is close to that predicted ($\Delta H^{\ddagger}$ 46.7 kcal/mol)[10] by subtraction of the allylic stabilization energy expected on replacement of methyl by vinyl (12.5 kcal/mol)[11] from the enthalpy of activation of the diastereomerization of 1,2-dideuterio-3-methylcyclopropane ($\Delta H^{\ddagger}$ 59.2 kcal/mol).[12] In terms of the criterion of concert which is based on the observed enthalpy of activation being *lower* than the predicted (by at least 3 kcal/mol to make reasonable allowances for uncertainties in estimated and experimental values), the ring enlargement appears to be no more obviously concerted than the diastereomerization of cyclopropane.[12]

Experimental confirmation of this conclusion is given by the failure of *cis*-1,2-dideuterio-3-vinylcyclopropane to rearrange faster to cyclopentene than it undergoes diastereomerization.[13] Although this behavior, as that of 1-cyano-2-isopropenylcyclopropane,[1] may be no more than the reflection of the greater ease of generating a transoid allylic radical,[10a,14] from which, in the first instance, the thermochemically improbable *trans*-cyclopentene is to be expected, it nonetheless implies a potential concert too feeble to muster the 1-kcal/mol extra cost of the cisoid configuration required for the realization of the concert.

Configurational characterization of the vinylcyclopropane rearrangement has already been afforded by the investigation of Willcott and Cargle.[13] Their "experimental result is consistent only with a mechanism in which stereochemistry is lost at two centers". The absence of stereospecificity excludes the operation of a single, concerted path preferred by 3 kcal/mol or more over the model of a stereorandom, energetically nonconcerted path.

Theoretical predictions of stereochemistry are mixed. Analysis according to Woodward and Hoffmann[15] favors $\sigma^2_a + \pi^2_s$ or $\sigma^2_s + \pi^2_a$ (the is and ra processes of Figure 1, respectively), whereas control by subjacent orbitals[16] favors processes rs and ia, respectively.

A complete configurational specification of the rearrangement can be achieved if both carbon atoms of the newly formed, cyclopentene-generating bond be chiral. This condition can be realized either by a diastereomeric or an enantiomeric marker, either through the introduction of a third chiral atom (e.g., if R = H and P ≠ Q ≠ S ≠ H in Figure 1) or optical activity (e.g., if P = R = H and Q ≠ S). The former approach has been pursued by Mazzocchi and Tamburin[17] (P = $-COOC_2H_5$, Q = S = CH_3 and R = H) but has resisted a definitive experimental expression, presumably owing to the kinetic complexity of the system.[18] Of the two approaches, optical activity seems the less perturbing (even should P be deuterium) and the more conducive to reliable quantitative assessment.

In the present work, the stereochemical characterization of the nonallylic carbon atom, that is, the relative amount

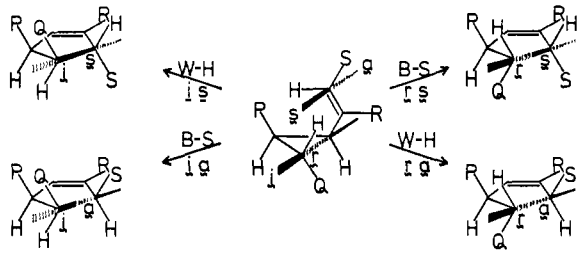


Figure 1. The four stereochemically distinguishable paths for the vinylcyclopropane rearrangement, after Mazzocchi and Tamburin.[17] The symbols, W-H and B-S, stand for Woodward and Hoffmann[15] and Berson and Salem,[16] respectively; s, a, i, and r stand for suprafacial, antarafacial, inversion, and retention, respectively.

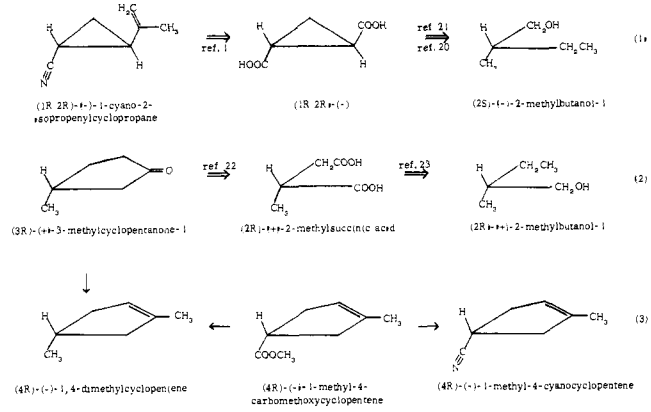


Figure 2. Outline of the configurational interrelationship between 1-cyano-2-isopropenylcyclopropane and 4-cyano-1-methylcyclopentene.

of inversion (i) and retention (r), has been determined. The stereochemistry of the allylic carbon, which has not been determined, is under active investigation.

For the present, more limited purpose, optically active *trans*- and *cis*-1-cyano-2-isopropenylcyclopropane are sufficient (P = S = H, Q = -CN, and R = $-CH_3$ in Figure 1). Their preparations and absolute configurational specifications as (1*R*,2*R*)-(−)-*trans*-I and (1*S*,2*R*)-(+)-*cis*-I have been effected in the earlier study[1] in which preliminary experiments, first on the methyl esters of the related carboxylic acids and later on the nitriles, revealed the retention of some optical activity in the cyclopentene product of rearrangement and gave encouragement to the quantitative assessment of the stereochemical course of the reaction.

The complete resolution of the problem presupposes evaluation of the specific rotation of optically pure 4-cyano-1-methylcyclopentene and establishment of the configurational relationship to the starting cyclopropanes.

Correlation of Configurations

The common point relating the configurations of (−)-*trans*- and (+)-*cis*-cyano-2-isopropenylcyclopropane (*trans*-I and *cis*-I) to that of 4-cyano-1-methylcyclopentene (II) is active amyl alcohol, (2*S*)-(−)-2-methylbutanol-1; the absolute configuration is assigned by Doering and Kirmse.[20] The interrelationship is outlined in eq 1 of Figure 2.

The configurationally relevant precursor of (−)-*trans*-I is (1*R*,2*R*)-(−)-*trans*-cyclopropanedicarboxylic acid.[1] This substance has been configurationally related to (1*R*,2*R*)-(−)-1,2-dimethylcyclopropane by Inouye, Sagita, and Walborsky,[21] which, in turn, has been related to (2*S*)-(−)-2-methylbutanol-1 by the method of carbene insertion.[20] Since (−)-*trans*-I and (+)-*cis*-I are configurationally related by base-catalyzed reversible epimerization, the absolute configurations of both are established.

In the assignment of absolute configuration to 4-cyano-1-methylcyclopentene (II), the reference substance is 3-methylcyclopentanone. Its dextrorotatory enantiomer has been obtained from (+)-pulegone, the configuration of which[22] is inferred from its degradation to (−)-α-methylglutaric acid by Eisenbraun and McElvain.[23] (+)-3-Methylcyclopentanone has also been converted to (*R*)-(+)-methylsuccinic acid, the chemical interrelationship of which to (2*R*)-(+)-2-methylbutanol-1 has been accomplished by Rossi, Diversi, and Ingrosso.[24] This sequence is sketched in eq 2 of Figure 2.

In the present work, the final connection to II is made by the sequence shown in eq 3 of Figure 2. In the first phase, (*R*)-(+)-3-methylcyclopentanone is related to (1*R*)-(−)-1,4-dimethylcyclopentene by treatment with methylmagnesium bromide followed by dehydration of the resulting alcohol. In the second phase, (4*R*)-(−)-4-cyano-1-methylcyclopentene is related to methyl (4*R*)-(−)-1-methylcyclopentene-4-carboxylate, which in turn is transformed into (4*R*)-(−)-1,4-dimethylcyclopentene. The absolute configurations of I and II are thus established.

The present work begins with 1-methylcyclopentene-4-carboxylic acid (III) which is obtained from diethyl 1-methylcyclopentene-4,4-dicarboxylate, a substance prepared according to the procedure of Schweizer and O'Neill.[25] Resolution of III with quinine affords a sample of (+)-III, $[\alpha]_{365}$ +65.2°, of unknown optical purity. Conversion to 1-methylcyclopentene-4-carboxamide, $[\alpha]_{365}$ +22.1°, followed by dehydration by means of *p*-toluenesulfonyl chloride and pyridine at 10° gives (+)-4-cyano-1-methylcyclopentene [(+)-II], $[\alpha]_{365}^{26}$ +47.2°. The methyl ester of (+)-III, $[\alpha]_{365}^{27}$ +71.1°, obtained from the same sample of (+)-III by treatment with diazomethane, is reduced with $LiAlH_4$ to the corresponding alcohol. Treatment, first with *p*-toluenesulfonyl chloride and second with $LiAlH_4$, affords (+)-1,4-dimethylcyclopentene, $[\alpha]_{365}^{27}$ +13.6°. An authentic sample, $[\alpha]_{365}^{27}$ −16.9°, is obtained from optically pure (*R*)-(+)-3-methylcyclopentanone, $[\alpha]^{26}D$ +155.4°, by treatment with methylmagnesium bromide followed by dehydration of the diastereoisomeric alcohols in the presence of a trace of acid.

If the sample of (*R*)-(+)-3-methylcyclopentanone derived from (+)-pulegone[22] is assumed to be optically pure, the derived sample of (+)-1,4-dimethylcyclopentene should also be optically pure. It can then be calculated, if a small correction is made for the difference in concentration at which the rotation is measured, that the sample of (+)-1,4-dimethylcyclopentene derived from (+)-III, $[\alpha]_{365}$ +65.2°, is 0.884 ± 0.008 of optical purity. The uncertainty derives from the accuracy (±0.002°) in the measurement of α, the observed rotation. If the same degree of optical purity is ascribed to the sample of partially resolved III, the specific rotation of optically pure (+)-4-cyano-1-methylcyclopentene [(+)-II] may be taken to be $[\alpha]_{365}^{26}$ +55.9 ± 0.5°.

Specific Rate Constants of Diastereomerization and Rearrangement

The kinetics of the thermal diastereomerization and the rearrangement to 4-cyano-1-methylcyclopentene (II) of *trans*-I and *cis*-I at 217.8° are determined by the procedures described previously.[1] The experimental data are given in Table I.

Four rate constants, k_1, k_2, k_3, and k_4, are defined in the kinetic scheme for a three-component system related by first-order processes[26] as shown in Figure 3. The formation of the cyclopentene (C) is considered to be irreversible, while the interconversion of *trans*- and *cis*-I is known to be reversible.[1] Values for the rate constants are extracted from these data by means of the integrated rate expressions[26] of

Table I. Kinetic Data for Thermal Isomerization of *trans*-I and *cis*-I in Gas Phase at 217.8°

Time, sec	*trans*-I		*cis*-I		II	
	Exptl[a] %	Calcd[b] %	Exptl[a] %	Calcd[b] %	Exptl[a] %	Calcd[b] %
0000[c]	99.48 ± 0.02		0.52 ± 0.01		0.000	0.000
2790	96.74 ± 0.02	96.76	3.13 ± 0.01	3.11	0.132 ± 0.004	0.126
5400	94.45 ± 0.03	94.41	5.31 ± 0.03	5.34	0.249 ± 0.006	0.253
9000	91.34 ± 0.15	91.53	8.12 ± 0.16	8.04	0.542 ± 0.010	0.434
13200	88.59 ± 0.14	88.61	10.77 ± 0.13	10.73	0.636 ± 0.013	0.655
18600	85.56 ± 0.03	85.44	13.53 ± 0.02	13.61	0.915 ± 0.007	0.953
0000[d]	0.0000	0.00	100.00	100.00	0.000	0.000
2760	6.89 ± 0.02	7.07	92.75 ± 0.03	92.55	0.361 ± 0.010	0.374
5490	13.19 ± 0.03	13.16	86.10 ± 0.03	86.13	0.709 ± 0.006	0.713
9000	20.31 ± 0.02	20.51	78.54 ± 0.04	78.34	1.152 ± 0.021	1.151
13200	28.04 ± 0.01	27.87	70.25 ± 0.01	70.50	1.713 ± 0.011	1.630
18600	35.72 ± 0.01	35.71	62.14 ± 0.01	62.09	2.136 ± 0.020	2.202

[a] The data, obtained by GLC analysis using a digital integrator, are the means of three analyses at each point and are used directly in the computer refinement with no implication about the accuracy. [b] The calculated values are obtained by the computer program for the kinetic model in Figure 3 using the mean of the best values for the four rate constants: $k_1 = 10.11$; $k_2 = 27.03$; $k_3 = 1.39$; and $k_4 = 0.44$ given in Table II. At these values of the rate constants, the error (defined as the sum of the squares of deviations between the calculated and experimental values of concentration for all the points) is 0.2504. [c] The run starting with *trans*-I. [d] The run starting with *cis*-I.

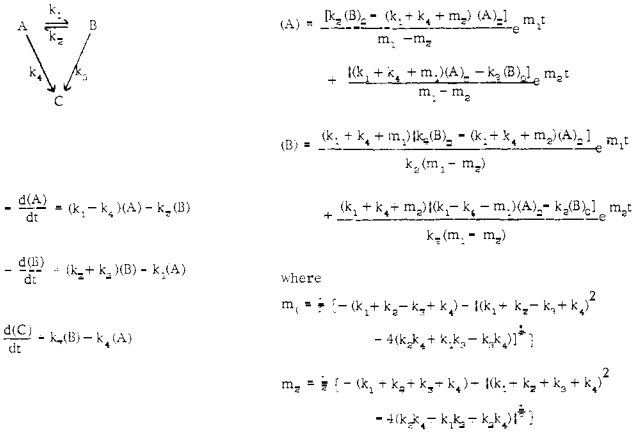


Figure 3. The kinetic model for diastereomerization and rearrangement to 4-cyano-1-methylcyclopentene (C) of racemic *trans*(A)- and *cis*(B)-1-cyano-2-isopropenylcyclopropane.

the differential equations describing the rate of change of concentration of the two components, A and B, with time. The boundary conditions are (A) = $(A)_0$, (B) = $(B)_0$, and (C) = 0 at $t = 0$, where A, B, and C refer to *trans*-I, *cis*-I, and II, respectively.

The concentration of the third component (C) is obtained from the relation (A) + (B) + (C) = $(A)_0 + (B)_0 + (C)_0$. Solution of these integrated rate equations for the theoretical values of the concentration of A, B, and C as a function of time for a given set of the four rate constants is achieved by a computer program in which the four parameters, k_1, k_2, k_3, and k_4, are varied within desired limits by specified increments until the best fit of the equations with the experimental data is achieved. In this manner, calculated values of (A), (B), and (C) are obtained for several combinations of the four parameters and compared with the experimental values for the corresponding time periods. The difference or the error is computed as the sum of the squares of the deviations at the five experimental points (Table I).

In order to calculate best values for the four rate constants using this iterative procedure, approximate values of these parameters are required as starting points. The values taken for k_1 ($9.98 \pm 0.03 \times 10^{-6}$ sec^{-1}) and k_2 ($27.36 \pm 0.07 \times 10^{-6}$ sec^{-1}) are from the earlier analysis[1] based on neglect of the formation of cyclopentene and on the rate expression for reversible first-order reactions of a two component system: $t(k_1 + k_2) = -\ln [(AK - B)/(A_0K - B_0)]$. Initial guesses of values for k_3 and k_4 are obtained by treating the formation of II as a first-order disappearance of *trans*-I (and *cis*-I). From the expression, $k = 1/t \ln [a/(a - x)]$, where a is the initial concentration of A (*trans*-I) or B (*cis*-I) depending on the starting material, and x is the amount of cyclopentene (II) formed at time t; the data in Table I are reduced by the method of least-squares to give $k_4 = 0.50 \pm 0.04 \times 10^{-6}$ sec^{-1} and $k_3 = 1.30 \pm 0.01 \times 10^{-6}$ sec^{-1}.

Table II. Rate Constants[a] at Minimum Deviations Based on the Data in Table I

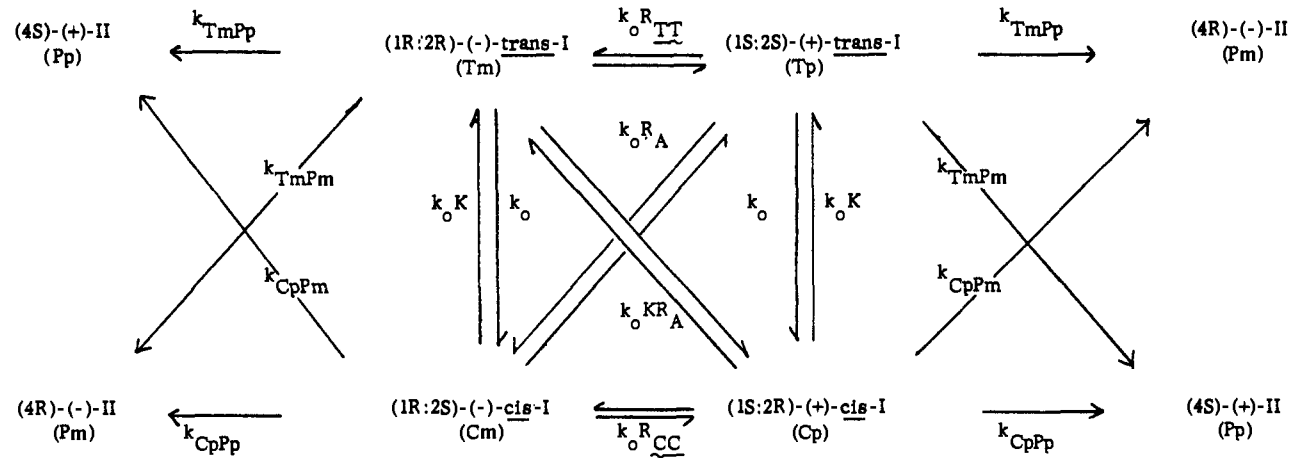
k_i	k_j			
	k_1	k_2	k_3	k_4
k_1	[10.11 ± 0.06][b]	27.026 ± 0.064	1.387 ± 0.054	0.44 ± 0.042
k_2	10.106 ± 0.056	[27.03 ± 0.06]	1.387 ± 0.054	0.44 ± 0.044
k_3	10.107 ± 0.060	27.022 ± 0.064	[1.39 ± 0.05]	0.44 ± 0.044
k_4	10.107 ± 0.067	27.030 ± 0.061	1.388 ± 0.052	[0.44 ± 0.04]

[a] All constants are in units of 10^{-6} sec^{-1}. [b] The values in brackets are the best values with their precisions as defined in the text.

All the data of Table I (taken from the preceding paper,[1] but now recalculated to include the formation of II) are handled simultaneously to avoid the relative insensitivity of (values of) k_3 to k_1 and k_4 to k_2 (and vice versa). In the first step, for a given value of k_i, two other k held constant, and an arbitrary value of k_j, the sum of the squares of the deviation between the calculated and observed values of the concentration of A, B, and C is determined. In the second step, k_j is varied over preset intervals until the value of k_j giving a minimum value of the deviation is identified. The lowest value among these minima is then determined by varying values of k_i. This procedure is then repeated for each of the other k's until best values of all four have been identified. Estimates of the relative precision of the four rate constants are made by giving the range of values of each constant which fall within 10% of the minimum deviation. The estimated precisions, the best-fit values, and the state of the iteration at the end are given in Table II. The calculated values of concentrations are compared directly with the experimental values in Table I.

Stereochemistry of the Rearrangement

Isomerization of (1*R*,2*R*)-(−)-1-cyano-2-isopropenylcyclopropane [(−)-*trans*-I] and its (1*S*,2*R*)-(+) epimer [(+)-*cis*-I], prepared as previously described,[1] is effected in the gas phase at 217.8°. The resulting 4-cyano-1-methylcy-



$k_o = 3.16(\alpha)$ $[R_A = 2.20]$ $k_o R_A = 6.95(\beta)$

$k_o K = 8.45(\delta)$ $[K = 2.67]$ $k_o KR_A = 18.58(\epsilon)$

$[R_{TT} = 2.23]$ $k_o R_{TT} = 7.03(\gamma)$

$[R_{CC} = 2.92]$ $k_o R_{CC} = 9.20(\zeta)$

Figure 4. Expansion of the four-variable scheme of Figure 3 to the complete nine-variable kinetic scheme, on the basis of which the experimental data are reduced to specific rate constants in units of $(10^6 \text{ sec})^{-1}$. Included are computer refined values of the constants.

clopentene [(+)-II] is optically active and, whether from (−)-*trans*-I or (+)-*cis*-I, is dextrorotatory.

Since, starting with (+)-*cis*-I, the rate of formation of II is 19 times slower than the rate of formation of *trans*-I and 15 times slower than the rate of racemization of (+)-*cis*-I (a similar situation prevails starting with (−)-*trans*-I), it is not experimentally feasible to obtain optical data sufficiently near the beginning of the reaction to make simple, linear extrapolation back to zero time reliable. With the quantities of material available (0.4-g sample of starting material), the earliest moment at which a sufficient sample (5 mg) could be collected, isolated, purified, and examined with acceptable accuracy is already beyond the time where a substantial amount of reaction has occurred. Thus, in a 630-min run with (−)-*trans*-I in which only 2.4% of II has been formed, racemization has already proceeded to the extent of 48.6%, and 19.4% of *cis*-I has been formed. Similarly, in a 434-min run with (+)-*cis*-I in which 3.1% of II has been produced, racemization amounts to 44.1%, and 43.2% of *trans*-I has been formed.

From (−)-*trans*-I of 89.6% optical purity, 4-cyano-1-methylcyclopentene (II), α_{365}^{27} +0.048 ± 0.002° (*c* 0.435, cyclohexane), corresponding to $[\alpha]_{365}^{27}$ +12.3° (corrected to starting material of 100% of optical purity), is produced. The optical purity of the sample of (+)-II is thus 22.0 ± 0.9% and corresponds to a ratio of 1.564 ± 0.030 in favor of the dextrorotatory enantiomer [61% of (+)-II and 39% of (−)-II].

From (+)-*cis*-I (of 100% optical purity), (+)-II shows α_{365}^{27} +0.037 ± 0.002 (*c* 0.423) and +0.056° (*c* 0.586, cyclohexane) which correspond to an average $[\alpha]_{365}^{27}$ +9.15°. The optical purity, 16.4 ± 0.9%, corresponds to a ratio of 1.392 ± 0.030 in favor of (+)-II [58% of (+)-II and 42% of (−)-II].

These ratios must be extrapolated to zero time to correct for product which has arisen from increasingly racemized starting material and diastereomer. It is to be noted that the latter is not more than 37% of optical purity even when generated at the beginning of reaction and becomes increasingly optically degraded as the reaction proceeds. If the uncontaminated optical characteristics of the rearrangement of (−)-*trans*-I and (+)-*cis*-I to II are to be known, the individual specific rate constants must be disentangled. This is particularly essential in the case of (−)-*trans*-I, where (+)-*cis*-I of 37% optical purity is formed 23 times faster than II and then rearranges to II nearly 3 times faster than does *trans*-I itself.

The Kinetic Ratio of (+)- to (−)-II

The complete kinetic description of the system (+)- and (−)-*trans*-I, (+)- and (−)-*cis*-I, and (+)- and (−)-II is shown in Figure 4. The assumptions of reversibility and irreversibility in this scheme are substantiated by experiment, as is the further assumption that irreversible leakage out of the system is negligible.

Approximate values for all the constants in the central square have already been reported by Doering and Sachdev[1] (see Figure 8 in that paper). The refined values developed in this work are given in Figure 4.[27]

The four individual specific rate constants required for the stereochemical characterization of the rearrangement of the cyclopropanes to the cyclopentenes are also shown in Figure 4. These can be defined in terms of the ratio, R_{TP}, of the specific rate constant for the formation of (4*S*)-(+)-II(Pp)[k_{TmPp}] to that of (4*R*)-(−)-II(Pm)[k_{TmPm}] from (1*R*,2*R*)-(−)-*trans*-I(Tm) and in terms of the specific rate constant for the conversion of *trans*-I to II [$k_{TP} = k_4$ of Figure 3]; similarly, the ratio, R_{CP}, of (4*S*)-(+)-II(Pp)[k_{CpPp}] to (4*R*)-(−)-II(Pm)[k_{CpPm}] from (1*S*,2*R*)-

(+)-*cis*-I(Cp) and the specific rate constant for conversion of *cis*-I to II [$k_{CP} = k_3$ of Figure 3].

Since $R_{TP} = k_{TmPp}/k_{TmPm}$ and $k_{TP} = k_{TmPp} + k_{TmPm} = 0.44\ (\eta)$,

$$k_{TmPp} = \eta R_{TP}/(R_{TP} + 1);\ k_{TmPm} = \eta/(R_{TP} + 1) \quad (1)$$

Similarly, $R_{CP} = k_{CpPp}/k_{CpPm}$ and $k_{CP} = k_{CpPp} + k_{CpPm} = 1.39\ (\vartheta)$,

$$k_{CpPp} = \vartheta R_{CP}/(R_{CP} + 1);\ k_{CpPm} = \vartheta/(R_{CP} + 1) \quad (2)$$

Expressions for the concentrations of the six components, (Pp), (Pm), (Tm), (Tp), (Cp), and (Cm), at reaction time, j, after reaction over one time interval, $j - i = \Delta t$, may be written in terms of the concentrations which existed at time, i:

$$(Pp)_j = (Pp)_i + [k_{TmPp}(Tm)_i + k_{TmPm}(Tp)_i + k_{CpPp}(Cp)_i + k_{CpPm}(Cm)_i]\Delta t \quad (3)$$

$$(Pm)_j = (Pm)_i + [k_{TmPm}(Tm)_i + k_{TmPp}(Tp)_i + k_{CpPm}(Cp)_i + k_{CpPp}(Cm)_i]\Delta t \quad (4)$$

$$(Tm)_j = (Tm)_i + [-(\eta + \alpha + \beta + \gamma)(Tm)_i + \gamma(Tp)_i + \epsilon(Cp)_i + \delta(Cm)_i]\Delta t$$

$$(Tp)_j = (Tp)_i + [\gamma(Tm)_i - (\eta + \alpha + \beta + \gamma)(Tp)_i + \delta(Cp)_i + \epsilon(Cm)_i]\Delta t$$

$$(Cp)_j = (Cp)_i + [\beta(Tm)_i + \alpha(Tp)_i - (\vartheta + \delta + \epsilon + \zeta)(Cp)_i + \zeta(Cm)_i]\Delta t$$

$$(Cm)_j = (Cm)_i + [\alpha(Tm)_i + \beta(Tp)_i + \zeta(Cp)_i - (\vartheta + \delta + \epsilon + \zeta)(Cm)_i]\Delta t$$

The specific rate constants in eq 3 and 4 can be replaced by their equivalents in eq 1 and 2. There being two experimental observations, one of $(R_{TP})_{37800sec} = 1.564 \pm 0.030$ starting from (−)-*trans*-I(Tm) and the other of $(R_{CP})_{26040sec} = 1.392 \pm 0.030$ starting from (+)-*cis*-I(Cp), it is possible to solve the equations for values of R_{TP} and R_{CP} at zero time [$(R_{TP})_0$ and $(R_{CP})_0$, respectively].

Based on this scheme, a computer program has been written in which guessed values for $(R_{TP})_0$ and $(R_{CP})_0$ in the rearrangement of (−)-*trans*-I and (+)-*cis*-I, respectively, and the observed values of the eight specific rate constants are converted into calculated values of the concentrations of (Tm), (Tp), (Cp), (Cm), (Pp), and (Pm) as a function of time. It is immaterial whether Δt is taken as $1/100$ of the total reaction time or $1/200$, that is, whether 100 or 200 steps are used in the calculation. From the calculated concentrations of (Pp) and (Pm), values of $(R_{TP})_{37800}$ and $(R_{CP})_{26040}$ are calculated and compared with the experimental values, the difference or the error being noted. By an iterative procedure, successive values of $(R_{TP})_0$ and $(R_{CP})_0$ are selected until the error $(R_{calcd} - R_{obsd}) \leq 0.001$.

Solutions are obtained when $(R_{TP})_0 = 2.27_2$ and $(R_{CP})_0 = 1.53_7$. These values correspond to initial ratios at time zero of (+)-II(Pp) to (−)-II(Pm) of 69.4:30.6 and 60.0:39.4, from (−)-*trans*-I(Tm) and (+)-*cis*-I(Cp), respectively. In order to obtain the best fit as a function of time of the equations in the kinetic scheme in Figure 4 with the experimental data[1] for the retention of optical activity in the starting material and in the product of its diastereomerization, the necessary readjustments in the previously reported[1] values of R_A, $k_{\alpha(C)}$, and $k_{\alpha(T)}$ are also made. With the final optimized values of the parameters, the concentration of each component is computed as a function of time, from which the enantiomeric purities of *trans*-I, *cis*-I, and II at zero time are determined. The calculated data along with the corresponding experimental values are given in Table III. The computed plots of the distribution of enantiomers among the products are shown in Figures 5 and 6.

Table III. Calculated[a] and Experimental[b] Optical Purity of (−)-*trans*-I, (+)-*cis*-I, and (+)-II

Time,[c] sec	(−)-*trans*-I		(+)-*cis*-I		(+)-II	
	Calcd	Exptl	Calcd	Exptl	Calcd	Exptl
2790	96.08	96.36	35.61	35.25	37.12	
5400	92.41	92.38	34.11	34.19	35.36	
9000	87.34	87.63	32.12	32.20	33.19	
13200	81.54	81.36	29.92	30.55	30.98	
18600	74.30	74.48	27.25	28.24	28.50	
37800	51.62	51.40	19.29	19.23	22.02	22.00
Time,[d] sec	(+)-*cis*-I		(−)-*trans*-I		(+)-II	
	Calcd	Exptl	Calcd	Exptl	Calcd	Exptl
2760	94.96	95.59	35.83	35.43	20.62	
5490	89.97	89.95	34.25	33.92	20.04	
9000	83.87	84.54	32.30	32.25	19.33	
13200	76.69	75.95	30.05	29.97	18.52	
26040	56.56	55.92	24.04	24.69	16.34	16.39

[a] The calculated values are obtained from the enantiomeric distribution computed as a function of time taking Δt as $1/100$ of the total reaction time starting with (−)-*trans*-I and (+)-*cis*-I. [b] For the experimental values of optical purity, data at 37800 sec starting with (−)-*trans*-I and 26040 sec starting with (+)-*cis*-I are obtained from the present studies, while the other data were obtained previously.[1] [c] Data starting with (−)-*trans*-I. [d] Data starting with (+)-*cis*-I.

The excellence of the agreement between the computer calculated curves and the experimental data gives considerable confidence in the reliability of the long extrapolation from the single experimental value of the enantiomeric ratios in the 4-cyano-1-methylcyclopentene back to zero time and the intrinsic ratios, R_{TP} and R_{CP}, derived from that extrapolation.

The configurational characterization of the rearrangement is summarized in Figure 7 in terms of retention and inversion (see Figure 1). The ratios, R_{TP} and R_{CP}, may be redefined as the ratios of rearrangement by retention (r) and inversion (i) $[R_{r/i}]_{trans} = 0.44$ and $[R_{r/i}]_{cis} = 1.54$, respectively.

The observed stereoselectivities, small though they be in contrast to those encountered in strongly concerted rearrangements like that of cyclobutene, remarkably have opposite senses in *trans*-I (inversion favored) and *cis*-I (retention favored). When it is further recognized that retention involves zero (or any even number of) rotations of the cyano group whereas inversion involves one (or any odd number of) rotation of the cyano group, the difference between the two processes is not trivial.

For related behavior, one can look neither to the work of Willcott and Cargle[13] nor to the elegantly conceived work of Mazzocchi and Tamburin[17] for further information on the relative importance of retention and inversion in the cyclopentene rearrangement (neither to the former because it was not originally intended that it bear on the question; nor to the latter, in some measure because of the extensive destruction of the ring by 1,5-hydrogen shifts, but, to a greater extent, because of the absence of information about direct interconversions among the four diastereomers). In unpublished work of Roth and Schmidt,[28] inversion of configuration appears to be favored in the rearrangement of both *trans*-1-methyl-2(*trans*-propenyl)cyclopropane and *cis*-1,2-dimethyl-*trans*-3-vinylcyclopropane to *trans*-3,4-dimethylcyclopentene.[29] However, at which carbon atom the inversion occurs cannot be specified.

These rearrangements of vinylcyclopropane to cyclopentene are significantly slower than the sum of the three com-

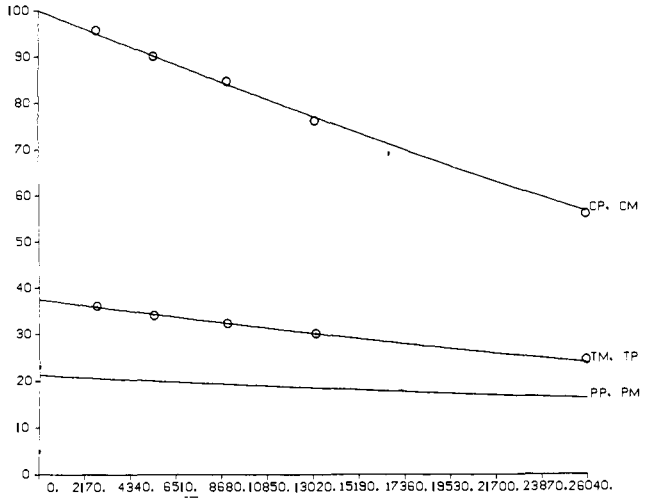


Figure 5. The points are the experimental optical purities expressed in percent of the major enantiomer, starting with Cp [(+)-*cis*-I], upper curve, the product Tm [(−)-*trans*-I] in the middle curve, and the product Pp [(+)-II] in the lower curve (single datum at 26040 sec). The computer generated curves are the source of the optical purities of *trans*-I and II at zero time.

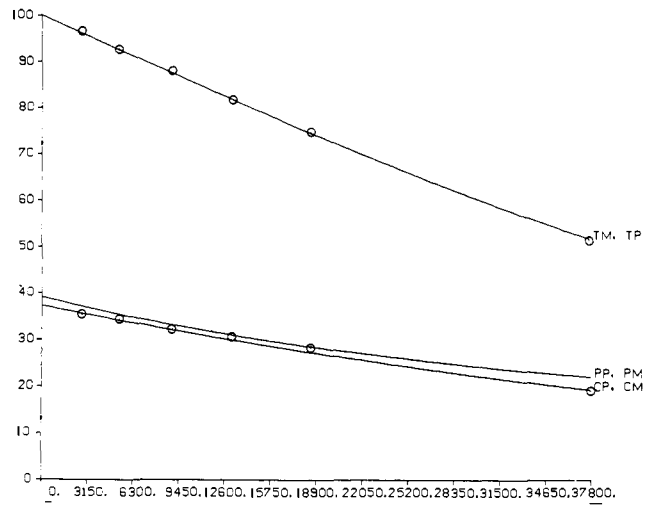


Figure 6. The points are the experimental optical purities expressed in percent of the major enantiomer, starting with Tm [(−)-*trans*-I], upper curve, the product Pp [(+)-II], middle curve (single datum at 37800 sec), and the product Cp [(+)-*cis*-I], lower curve (to which all encircled experimental points refer). The computer generated curves are the source of the optical purities of *cis*-I and II at zero time.

peting reactions: enantiomerization and the two enantiomeric diastereomerizations (see Table II). Thus, formation of cyclopentene amounts to 2.5% (of the total reactions) of *trans*-I and 3.8% of *cis*-I. More significant is the slowness of the cyclopentene rearrangement relative to enantiomeric diastereomerization: 4.35% as fast in the case of *trans*-I, and 5.14% in the case of *cis*-I.

The slowness, which corresponds to a value of $\Delta\Delta G^{\ddagger} \sim 3.0$ kcal/mol, finds good analogy in the series dihydrobullvalene (E_a = 12.6 kcal/mol),[30] *cis*-1,2-divinylcyclopropane (E_a = 20.0 kcal/mol),[31] and *cis*-3,3-dimethyl-1,2-divinylcyclopropane (E_a = 25.4 kcal/mol).[32] This series of Cope rearrangements can be interpreted as the revelation of an increasing steric opposition by substituents at the 3-position of the ring to the assumption of the cisoid configuration. A similar indication is provided by the observation of Ullenius, Ford, and Baldwin[33] that *trans*-1,2-bis(*cis*-prop-1-enyl)cyclopropane isomerizes reversibly to the cis isomer much faster than *cis*-3,4-dimethylcyclohepta-1,5-diene is

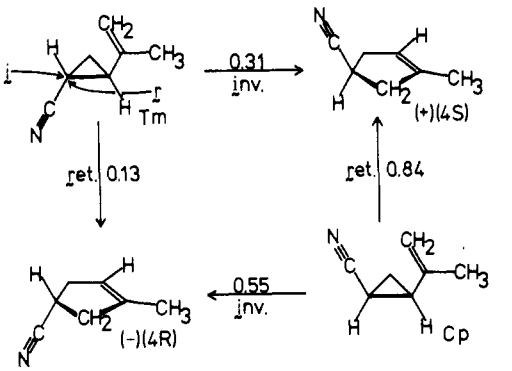


Figure 7. The partial reaction of (1*R*,2*R*)-(−)-*trans*-I(Tm) and (1*S*, 2*R*)-(+)-*cis*-I(Cp) to (4S)-(+)-II(Pp) and (4R)-(−)-II(Pm) at 217.8° in the gas phase. Specific rate constants are in units of $(10^6 \text{ sec})^{-1}$; retention and inversion are indicated by r and i, respectively.

produced. The activation energy for this Cope rearrangement, which requires a transition state in the cis conformation, can be estimated to lie more than 15 kcal/mol above that for unsubstituted *cis*-1,2-divinylcyclopropane. A similar observation has been made by Sasaki, Eguchi, and Ohno.[34]

The energy criterion for concert seems securely satisfied when the enthalpy of activation predicted for a nonconcerted model ($\Delta H^{\ddagger}_{\text{pred}}$) exceeds the experimental enthalpy of activation ($\Delta H^{\ddagger}_{\text{exptl}}$) by 3 or more kcal/mol (on the assumption of the commonly encountered uncertainties). The arguments in the application of this criterion revolve mainly around the level of uncertainty in the value of the predicted enthalpy of activation. Conclusive applications are found in rearrangements such as that of cyclobutene [($\Delta H^{\ddagger}_{\text{pred}}$ = 61.2) − ($\Delta H^{\ddagger}_{\text{exptl}}$ = 31.7) = 29.5 kcal/mol] or the 1,5-hydrogen migration in dienes [($\Delta H^{\ddagger}_{\text{pred}}$ = 95 − 1.5(12.5) = 76.3) − ($\Delta H^{\ddagger}_{\text{exptl}}$ = 35.4) = 41 kcal/mol].[19] An inconclusive application is found in the rearrangement of vinylcyclopropane under scrutiny here. Although the activation parameters for the thermal reactions of 1-cyano-2-isopropenylcyclopropane have not been determined as yet, it may be assumed that the log A factor will fall in the range 13.78 ± 0.53 shown by the 19 vinylcyclopropane rearrangements listed by Willcott, Cargill, and Sears.[4] The sum of the rate constants for interconversion of cis and trans, 38.97 × 10^{-6} sec^{-1}, at 217.8°, can then be used to extract a range of estimated enthalpies of activation, $\Delta H^{\ddagger}$ = 39.9 ± 1.2 kcal/mol. A predicted enthalpy of activation can be derived by subtraction of enthalpy lowering associated with replacement of hydrogen by cyano (8.0 kcal/mol)[38] from the experimental enthalpy of activation of the rearrangement of vinylcyclopropane.[9] The predicted enthalpy of activation, $\Delta H^{\ddagger}$ = 40.5 kcal/mol, is sufficiently close to that estimated from the specific rate constant to conclude that the rearrangement belongs to the not obviously concerted class.

The theoretical counterpart of the comparison of experimental with predicted enthalpy of activation as a criterion of concert has been outlined in the previous paper.[1] This criterion depends on having at least one among the competitive reactions proceed unavoidably by way of a transiently orthogonal diradical and thus to serve as a reference reaction which cannot be concerted in principle. In the present instance, diastereomerization serves as such a not-concerted-in-theory internal standard of reference. Since it involves a rotation of 180° of one carbon atom vis-à-vis another at some point during the geometrical transformation, it can be assumed, on the same theoretical basis underlying the Woodward-Hoffmann[15] and Berson-Salem[16] treatment of concert, that a point must be passed where the two

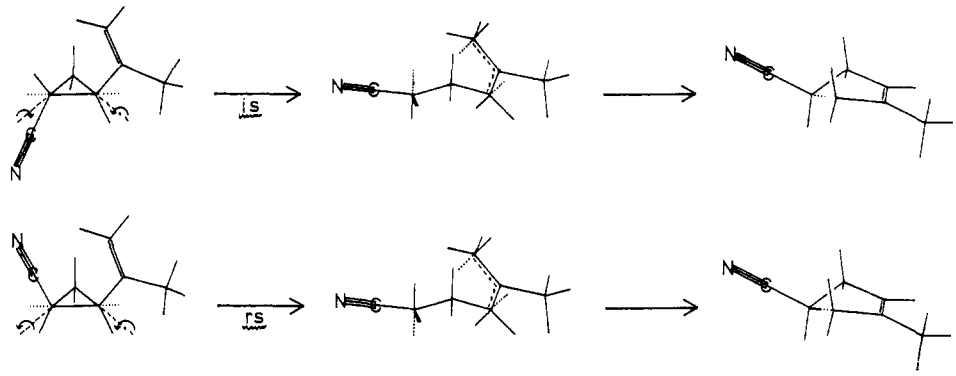


Figure 8. Representations of the hypothetical continuous diradicals as transition state in ring enlargement in their sterically favored directions.

p orbitals are orthogonal and do not interact in direct, through-space, energy-lowering overlap. To the extent that the slowness of the cyclopentene rearrangement relative to the diastereomerization may be ascribed to a higher enthalpy of activation and not a higher entropy of activation, this cyclopentene rearrangement may be concluded also to be not concerted.

The processes allowed by the conservation of orbital symmetry[15] are inversion–suprafacial (is) and retention–antarafacial (ra), whereas those allowed under control of subjacent orbitals[16] are inversion–antarafacial (ia) and retention–suprafacial (rs). Until present studies to elucidate the antarafacial–suprafacial dissection have been completed, the observed stereochemistry can only be discussed tentatively.

The lack of stereospecificity and the relative slowness give little encouragement to the hypothesis that direct orbital overlap is the dominant factor in the rearrangement of vinylcyclopropane to cyclopentene. That the values of $R_{r/i}$ should be less than 1.00 from (−)-*trans*-I and greater than 1.00 from (+)-*cis*-I finds no obvious explanation in terms of conservation of orbital symmetry (Figure 7). The hypothesis of a common intermediate, particularly when formulated as a freely rotating diradical, is clearly inadequate. In terms of the recently advanced, conceptual scheme of the continuous diradical as transition state, a significant role is ascribed to the internal rotations or torsions requisite to the realizations of the reactions. Although quite recent theoretical work holds promise of elucidating the factors governing rotational preferences,[39] empirical generalizations are still lacking.

We are struck by how close the observed rotational preferences, $[R_{i/r}]_{trans} = 2.27$ and $[R_{r/i}]_{cis} = 1.54$, are to the rotational preference of cyano over isopropenyl in the diastereomerization, $R_A = 2.20$. If the stereoselectivities are dominated by the preference of cyano to rotate and, furthermore, of cyano to rotate outward away from the sterically more crowded scene of the action, then the continuous diradical as transition state may reasonably be formulated as an outward rotation of the cyano group concluded by suprafacial bond formation with the allylic carbon atom (Figure 8). A large favoring of rotation of the cyano group in one direction over the other is scarcely to be expected since the extension of the vibration leading to reaction involves a separation of 2.5 Å or more at which point not much room is left for large steric interactions.

Such a speculative explanation at least encompasses the fact that inversion predominates in the rearrangement of the trans diastereoisomer, while retention predominates in that of the cis diastereoisomer.

Experimental Section

Optical rotations were determined on a Perkin-Elmer 141 digital readout polarimeter which has an accuracy of ±0.002°. Where knowledge of the accuracy of a measurement is particularly important, the observed rotation, α, is reported in parentheses following the specific rotation. NMR spectra were recorded in deuteriochloroform (unless indicated otherwise) on Varian A-60 and T-60 spectrometers, and the chemical shifts are reported in parts per million 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 gas chromatograph. Relative areas of GLC peaks were determined with a Digital Integrator Autolab Model 6300. Purification and separation of larger quantities was accomplished by preparative GLC on Autoprep Model A-700. The following columns were employed: column A, K-20M Perkin-Elmer, 300 ft × 0.01 in. capillary column (He flow 1–2 ml/min); column B, 13.5 ft × 0.25 in., 10% Carbowax 20M on 70–80 Anakrom ABS; column C, 28 ft × 0.25 in., 16% Carbowax 600 + 8% $AgBF_4$ on Chromosorb P.

Mass spectral analyses were made with an AEI Model MS 9 double-focusing mass spectrometer. Microanalyses were executed by Scandinavian Microanalytical Lab, Herlev, Denmark.

Computations were carried out on the Digital PDP-11 and the CALCOMP 565.

Thermal Isomerization of (−)-*trans*-I. Isolation of (+)-4-Cyano-1-methylcyclopentene (II). Samples of (−)-*trans*-I ($[\alpha]^{27}D$ −182°, 89.6% optical purity; 0.39 g prepared according to Doering and Sachdev[1]) were transferred into Pyrex ampoules, 20 × 1.25 cm with a 10 × 0.6 cm tubing at the open end, degassed, and sealed under reduced pressure (10^{-4} mm). After being heated for 630 min at 217.8°, the products from all the ampoules were combined and analyzed by GLC on column A at 130°. Three peaks with retention times 29, 32, and 42 min (He flow, 1–2 ml/min) in the ratio 78.16:2.43:19.41 corresponding to *trans*-I, II, and *cis*-I, respectively, were revealed. Separation by preparative GLC on column B at 135° followed by repeated chromatography of the second and third fractions afforded, in addition to the starting material, (−)-*trans*-I of 51.4% retention of optical purity ($[\alpha]^{27}D$ −93.6° (*c* 0.5115, cyclohexane)), 5 mg of II ($[\alpha]_{365}^{27}$ +11.03° (+0.048 ± 0.002°, *c* 0.435, cyclohexane)) and 58 mg of *cis*-I ($[\alpha]_{365}^{27}$ −9.17° (−0.145°, *c* 1.5808, cyclohexane)). In order to determine the optical purity of this sample of (−)-*cis*-I more accurately, it was converted to (−)-*trans*-I by the procedure of base-catalyzed equilibration described before:[1] $[\alpha]^{27}D$ −35.3° (−0.313°, *c* 0.8875, cyclohexane); 19.4% of optical purity.

Thermal Rearrangement of (+)-*cis*-I. Isolation of (+)-II. A 0.3-g sample of (+)-*cis*-I, $[\alpha]^{27}D$ +4.4°, $[\alpha]_{365}^{27}$ −49.7° (−0.354°, *c* 0.7115, cyclohexane), obtained from (−)-*trans*-II, $[\alpha]^{27}D$ −202.5° (*c* 0.6290, cyclohexane), by base-catalyzed equilibration,[1] was sealed into Pyrex ampoules as described above and heated at 217.8° for 434 min. Analysis of the combined product on column A at 130° revealed three peaks corresponding to *trans*-I, II, and *cis*-I at 29, 32, and 42 min (He flow, 1–2 ml/min) in the ratio 43.24:3.06:53.70, respectively. Preparative GLC on column B at 135° yielded 6 mg of II, ($[\alpha]_{365}^{27}$ +9.56° (0.056°, *c* 0.586, cyclohexane), $[\alpha]_{365}^{27}$ +8.74° (0.037°, *c* 0.423, cyclohexane)), 0.102 g of *trans*-I ($[\alpha]^{27}D$ −50.1° (*c* 1.6665, cyclohexane), 24.7% retention of optical purity), and recovered *cis*-I ($[\alpha]_{365}^{27}$ −29.0° (−0.537°, *c* 1.8532, cyclohexane); optical purity (55.9%), determined by its conversion to (−)-*trans*-I, ($[\alpha]^{27}D$ −113.24° (*c*

0.5996, cyclohexane)).

***R*-(+)-3-Methylcyclopentanone.** A sample obtained from Aldrich Chemical Co. was purified by GLC on column B at 115°: $[\alpha]^{25}D$ +155.4° (+1.505°, *c* 0.9685, $CHCl_3$) [reported[22] $[\alpha]D$ +154.8° ($CHCl_3$)]. The identity of this sample was confirmed by ir, NMR, and mass spectra.

1,3-Dimethyl-1-cyclopentanol. To a solution of methylmagnesium bromide prepared from 0.3 g (25% excess) of magnesium metal and methyl bromide (excess) in anhydrous ether (40 ml), there was added dropwise a solution of (+)-3-methylcyclopentanone (0.97 g, 10 mmol) in 30 ml of ether. The mixture was heated under reflux for 2 hr and worked in the usual manner to afford 1,3-dimethyl-1-cyclopentanol as a diastereomeric mixture in quantitative yield. A sample of this product was collected by gas chromatography on column A at 110°: NMR δ 0.95–1.1 (pr of d, 3 H); 1.36 (pr of s, 3 H); 1.4–2.6 (unresolved m with an overlapping sharp s, 8 H). Gas chromatographic separation of the diastereomers by GLC was not attempted.

***R*-(−)-1,4-Dimethylcyclopentene and *R*-(+)-1,3-Dimethylcyclopentene.** The above mixture of cyclopentanols was treated with a trace of concentrated H_2SO_4 at 60°, while the products were distilled into a Dry Ice trap as formed. The mixture of olefins was separated by preparative gas chromatography on column C at 55° into two peaks of retention time 12 and 14 min (He flow, 25 ml/min), respectively, in nearly equal amounts.

1,4-Dimethylcyclopentene had: $[\alpha]^{27}D$ −8.5°, $[\alpha]_{365}^{27}$ −16.92° (−0.164°, c 0.9690, cyclohexane), and $[\alpha]_{365}^{27}$ −16.02° (−0.349°, *c* 2.1782, cyclohexane); NMR (CCl_4) δ 1.01 (d, J = 6 Hz, 3 H), 1.66 (m, 3 H), 1.7–2.86 (broad unresolved m, 5 H), 5.13 (partially resolved m, 1 H); ir 3040, 2961, 2919, 2338 (C—H), 1450 (m, C=C), 1380 cm^{-1} (m); exact mass (calcd for C_7H_{12}, 96.0938) 96.0934.

1,3-Dimethylcyclopentene had: $[\alpha]^{27}D$ +139.9° (*c* 1.1487, cyclohexane); NMR (CCl_4) δ 0.97 (d, J = 7 Hz, 3 H), 1.66 (unresolved m, 3 H), 1.13–1.93 (m, 2 H), 2.16 (m, 2 H), 2.66 (broad m, 1 H), 5.15 (partially resolved m, 1 H); ir 3025, 2950, 2940, 2855, 2835 (s, C—H), 1450 cm^{-1} (m, C=C).

1-Methylcyclopentene-4-carboxylic Acid. Diethyl 1-methylcyclopentene-4,4-dicarboxylate was prepared by following the procedure of Schweizer and O'Neill.[25] Diethyl (2-oxopropyl)malonate, prepared according to Hurd and McAuley,[40] bp 98–102° (1.5 mm) [reported[40] bp 110–111° (2–4 mm)], was treated with vinyltriphenylphosphonium bromide[41] to give diethyl 1-methylcyclopentene-4,4-dicarboxylate, bp 105° (1–2 mm) [reported[25] bp 95° (0–5 mm)]. This ester was saponified with KOH to the corresponding dicarboxylic acid in 96% yield [mp 117°; NMR δ 1.85 (d, 3 H), 3.15 (broad s, 4 H), 5.3 (unresolved m, 1 H), 13.63 (sharp s, 2 H)] which was decarboxylated by heating in pyridine at 105–110° for 5 hr. Removal of pyridine under reduced pressure yielded a residue which was poured over ice, acidified with 4 *N* HCl, and extracted with ether. The ether extracts were dried and concentrated to afford 1-methylcyclopentene-4-carboxylic acid (95%) as a colorless oil: NMR δ 1.7 (d, 3 H), 2.6 (complex m, 4 H), 3.13 (m, 1 H), 5.2 (m, 1 H), 12.21 (s, 1 H).

The corresponding methyl ester, obtained by treatment with ethereal diazomethane, was purified by gas chromatography on column B at 120°. The NMR spectrum was similar to that of the acid except for replacement of the signal at δ 12.21 by a resonance at 3.7 (s, 3 H).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.4; H, 8.6. Found: C, 68.5; H, 8.6.

4-Hydroxymethyl-1-methylcyclopentene. A solution of the above 4-carbomethoxy-1-methylcyclopentene (0.4 g, 2.7 mmol) in ether (20 ml) under a nitrogen atmosphere was added to a stirred suspension of lithium aluminum hydride (0.2 g, excess) in anhydrous ether (30 ml). The mixture was heated under reflux for 2 hr, cooled in ice, and treated with a saturated NH_4Cl solution (2.5 ml). The ether layer was decanted, and the residue was extracted twice with ether. The combined extracts were dried ($MgSO_4$) and concentrated to yield 0.35 g of 4-hydroxymethyl-1-methylcyclopentene, of which a sample was purified by preparative GLC on column B at 135°: NMR δ 1.68 (unresolved m, 3 H), 1.9–2.63 (broad m, 5 H), 2.95 (sharp s, 1 H), 3.48 (d, J = 6 Hz, 2 H), 5.23 (unresolved m, 1 H).

1,4-Dimethylcyclopentene. A solution of the hydroxymethyl derivative (0.32 g, 3 mmol) in 1.5 ml of dry pyridine was cooled to −5°, treated with *p*-toluenesulfonyl chloride (0.55 g) in small lots over a 15-min period, stirred for 10 hr at 0°, poured over ice, and extracted with 50 ml of ether. Washing with 10% HCl to remove excess pyridine, drying over $MgSO_4$, and removal of solvent afforded 0.62 g (77%) of 1-methyl-4-*p*-toluenesulfomethylcyclopentene.

To a stirred suspension of lithium aluminum hydride (0.3 g, large excess) in 30 ml of anhydrous ether was added dropwise a solution of the *p*-toluenesulfonyl derivative (0.62 g) in ether (20 ml) under a nitrogen atmosphere. The mixture was heated under reflux for 3 hr and worked by a procedure similar to that described above for the reduction of the methyl ester, except that the solvent was removed by a careful distillation under a 10-cm Vigreux column (in order to minimize loss of the volatile product) until the volume was reduced to about 1 ml. Purification by preparative GLC on column C at 42° yielded a sample of 1,4-dimethylcyclopentene, the NMR spectrum of which was identical with that of the sample obtained from (+)-3-methylcyclopentanone.

Resolution of 1-Methylcyclopentene-4-carboxylic Acid. A suspension of quinine (4.2 g, 12.7 mmol) in 25 ml of ethyl acetate was combined with a solution of 1-methylcyclopentene-4-carboxylic acid (1.6 g, 12.7 mmol) in 15 ml of the same solvent. When stored at room temperature for 20 hr, the solution deposited 1.5 g of the quinine salt, two recrystallizations of which from ethyl acetate furnished 1.01 g of colorless crystals: mp 135° after being dried over P_2O_5 in vacuo; $[\alpha]^{27}D$ −135.5° (*c* 0.5329, MeOH).

Anal. Calcd for $C_{27}H_{34}N_2O_4$: C, 72.0; H, 7.6; N, 6.2. Found: C, 72.0; H, 7.8; N, 6.3.

Fractional crystallization of the material obtained from the filtrates afforded 0.45 g of the salt of the same optical purity. The combined samples were suspended in water, acidified with ice-cold 3 *N* HCl to pH 2 and extracted with three 30-ml portions of ether. The extract was dried over $MgSO_4$ and concentrated by distillation to give 0.4 g of the acid: $[\alpha]^{27}D$ +21.2°, $[\alpha]_{365}^{27}$ +65.2° (0.530°, *c* 0.8130, absolute EtOH). The corresponding methyl ester, 4-carbomethoxy-1-methylcyclopentene, obtained by treatment with ethereal diazomethane, was purified by GLC on column B: $[\alpha]^{27}D$ +22.9; $[\alpha]_{365}^{27}$ +71.1° (+0.606°, *c* 0.8526, MeOH); NMR identical with that of the racemic sample described above.

(+)-1,4-Dimethylcyclopentene. The above sample of (+)-4-carbomethoxy-1-methylcyclopentene was converted to the *p*-toluenesulfonyl derivative according to the procedure described above for the racemic material. Reduction with lithium aluminum hydride followed by preparative GLC on column C at 45° yielded (+)-1,4-dimethylcyclopentene: $[\alpha]^{27}D$ +6.9°, $[\alpha]_{365}^{27}$ +13.68° (+0.262°, *c* 1.9155), $[\alpha]_{365}^{27}$ + 13.61 (+0.263°, *c* 1.9318); $[\alpha]_{365}^{27}$ +13.26° (+0.184°, *c* 1.388), all in cyclohexane; NMR and ir identical with the sample ($[\alpha]_{365}^{27}$ −16.9°) obtained from *R*-(+)-3-methylcyclopentanone.

(+)-1-Methylcyclopentene-4-carboxamide. A solution of 0.115 g of 1-methylcyclopentene-4-carboxylic acid ($[\alpha]^{27}D$ +21.2°) in 15 ml of chloroform containing 0.101 g (1 mmol) of triethylamine was added dropwise with stirring to a solution of 0.108 g (1 mmol) of ethyl chloroformate in 15 ml of chloroform cooled to −25°. After the mixture had been stirred for 1 hr at −20 to −5°, NH_3 was bubbled through for 5 min. After a 1-hr period of further stirring at 25°, the precipitated material was filtered and washed twice with chloroform (20 ml). The combined extracts were washed with water, dried over $MgSO_4$, and concentrated under reduced pressure to give 0.1 g of a colorless solid. One crystallization from ether–petroleum ether furnished colorless (+)-1-methylcyclopentene-4-carboxamide: mp 130–131°; $[\alpha]^{27}D$ +8.6°, $[\alpha]_{365}^{27}$ +22.1° (+0.159°; *c* 0.7190, MeOH); NMR δ 1.73 (m, 3 H), 2.57 (4 H), 3.03 (m, 1 H), 5.28 (unresolved m, 1 H), 5.45–6.65 (2 H); ir 1675 cm^{-1} (s, $-CO—NH_2$).

(+)-4-Cyano-1-methylcyclopentene. To a solution of the above amide (0.09 g, 0.72 mmol) in dry pyridine (0.15 ml) was added dropwise a solution of *p*-toluenesulfonyl chloride (0.15 g, 0.8 mmol) in pyridine (0.2 ml) at 10°. After having been stirred for 8 hr at 20°, the mixture was diluted with anhydrous ether (20 ml) and stirred for 5 min. Precipitated material was removed by filtration and washed with ether (10 ml). The combined ethereal solution was washed with 1 *N* HCl until the aqueous extract was weakly acidic, dried over $MgSO_4$, and concentrated by distillation. Preparative GLC of the residue on column B at 140° afforded 40 mg of (+)-4-cyano-1-methylcyclopentene: $[\alpha]^{27}D$ +17.2°, $[\alpha]_{365}^{26}$

+47.2° (0.233°; c 0.494, cyclohexane); NMR and ir identical with those of the sample isolated from the thermal rearrangement of (−)-*trans*-I and (+)-*cis*-I.

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