Stereochemistry of the Thermal Isomerizations of (1*R*,2*S*)-1-(*E*-1-Propenyl)-2-phenylcyclopropane to 3-Methyl-4-phenylcyclopentenes

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When (1*R*,2*S*)-*trans*-1-(*E*-1-propenyl)-2-phenylcyclopropane is heated at 234.4 °C in the gas phase, it is isomerized reversibly to its (1*S*,2*R*) enantiomer and to the enantiomers of *cis*-1-(*E*-1-propenyl)-2-phenylcyclopropane as the four isomers of 3-methyl-4-phenylcyclopentene are formed more slowly. Kinetic and stereochemical evidence indicates that this vinylcyclopropane to cyclopentene rearrangement takes place with the participation of all four possible stereochemically distinct reaction paths: the relative contributions are 44% si, 20% ar, 25% sr, and 11% ai. This stereochemical pattern is substantially similar to those determined previously for the rearrangements of three chiral *trans*-1-alkenyl-2-methylcyclopropanes, a result reinforcing the perception that the stereochemistry of the rearrangement is controlled neither by orbital symmetry factors nor by the relative moments of inertia or radical-stabilizing capacities of substituent groups.

Introduction

The thermal rearrangement of vinylcyclopropane to cyclopentene[1] has become a reliable and versatile synthetic transformation[2] even as it has eluded a definitive mechanistic characterization.[3] With the advent of orbital symmetry theory the stereochemical aspects of this prototypical [1,3] carbon sigmatropic rearrangement gained prominent attention, for they could be expected to reveal its essential mechanistic nature. Of the four possible paths involving allylic participation with suprafacial (s) or antarafacial (a) stereochemistry, and [1,3] carbon migration with inversion (i) or retention (r), only two, the si and ar modes, may be classed as symmetry allowed. The other two, the sr and ai paths, cannot lead to cyclopentene products in a symmetry-allowed fashion.[4]

No published work has appeared reporting an experimental test of these clear predictions, a lacuna of reaction stereochemical fact one may readily appreciate, for Willcott and Cargle found that deuterium-labeled vinylcyclopropanes suffer thermal stereomutations very much faster than they are converted to cyclopentenes.[5] For other substituted cyclopropanes, the same difficulty intrudes: under thermal reaction conditions, specifically situated deuterium labels or other stereochemical markers on the cyclopropane reactant lose stereochemical integrity long before appreciable amounts of cyclopentene products may be formed.

In only three cases has it been possible to decipher the full stereochemical pattern defined by the relative rate constants for all four stereochemical paths of a vinylcyclopropane to cyclopentene rearrangement.[6-8] For these three published instances, the pattern of rate constants is remarkably insensitive to the substituent on the vinyl group. Scheme 1 summarizes these patterns by listing the percentages each k_{si}, k_{ar}, k_{sr}, and k_{ai} rate constant contributes to the total rate constant for rearrangement of a vinylcyclopropane to the isomeric cyclopentene.

All of these examples involve *trans*-1-alkenyl-2-methylcyclopropanes. These systems are experimentally tractable because stereomutations leading to *cis*-1-alkenyl-2-methylcyclopropanes lead on rapidly to acyclic dienes by way of a retroene hydrogen transfer,[9] and thus all cyclopentene products are derived from the two enantiomers of a trans reactant. By following the first-order loss of a chiral trans substrate as it gives mostly diene and very small amounts of cyclopentenes, and the first-order reduction of enantiomeric excess of the trans substrate, one may calculate weighted ee values for the trans reactant at any reaction time and then calculate from observed cyclopentene product ratios the relative magnitudes of k_{si}, k_{ar}, k_{sr}, and k_{ai}.[6-8]

The present work addressed the stereochemical aspects of another class of rearrangement of vinylcyclopropanes to cyclopentenes, employing a substrate having a phenyl at C2. (1*R*,2*S*)-1-(*E*-1-Propenyl)-2-phenylcyclopropane, (1*R*,2*S*)-**2-t**, was selected for study to learn how a more massive substituent with a larger moment-of-inertia and

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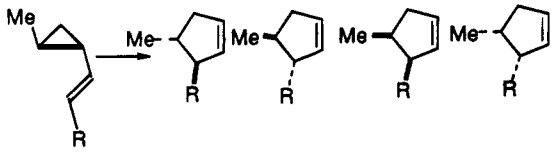
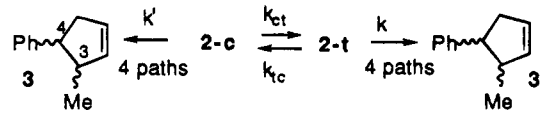
Scheme 1



	si	ar	sr	ai
1a, R = D:	55	15	18	13
1b, R = Me:	65	8	22	5
1c, R = Ph:	60	10	19	11

Scheme 2



better radical stabilizing capacities at C2 would change the relative magnitudes of the four rate constants for rearrangements to the four isomers of 3-methyl-4-phenylcyclopentene. From reports on the thermal reactions of *trans*-1-vinyl-2-phenylcyclopropane[10,11] and of the chiral forms of the cis and trans isomers of 1-isopropenyl-2-phenylcyclopropane[12] one may anticipate that the thermal cis,trans isomerization and enantiomerization of (1*R*,2*S*)-**2-t** will be much faster than the structural isomerizations giving 3-methyl-4-phenylcyclopentenes. In this system, then, one must learn how to gain the stereochemical facts even though the cis,trans isomerization of substrate is both rapid and reversible, its optical activity decays quickly, and some cyclopentene products may possibly be formed from *cis*-1-(*E*-1-propenyl-2-phenylcyclopropanes.

The kinetic situation in the absence of concern for optical activity is relatively simple (Scheme 2).

In Scheme 2, **2-t** = [*rac*-**2-t**], and similarly **2-c** stands for the sum of concentrations of both enantiomers of *cis*-1-(*E*-1-propenyl)-2-phenylcyclopropane; $k = (k_{si} + k_{ar} + k_{sr} + k_{ai})$ and $k' = (k_{si}' + k_{ar}' + k_{sr}' + k_{ai}')$. The first-order differential equations for the trans and cis isomers (eqs 1, 2) corresponding to this kinetic scheme may be readily solved if the constant coefficients are known.[13] The time dependence of [**2-t**] is a function of three experimentally definable variables: $[\mathbf{2\text{-}t}, \%] = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t)$; with $(A_1 + A_2) = [\mathbf{2\text{-}t}]$ at $t = 0$.

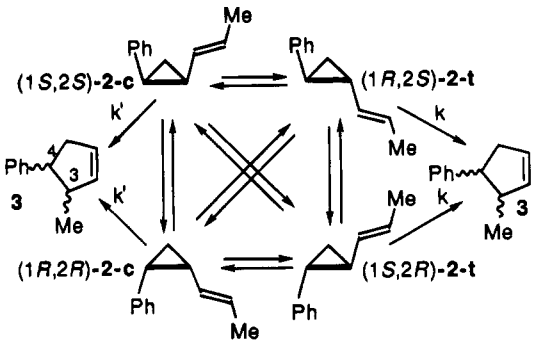
$$d[\mathbf{2\text{-}t}]/dt = -(k + k_{tc})[\mathbf{2\text{-}t}] + (k_{ct})[\mathbf{2\text{-}c}] \quad (1)$$

$$d[\mathbf{2\text{-}c}]/dt = (k_{tc})[\mathbf{2\text{-}t}] - (k' + k_{ct})[\mathbf{2\text{-}c}] \quad (2)$$

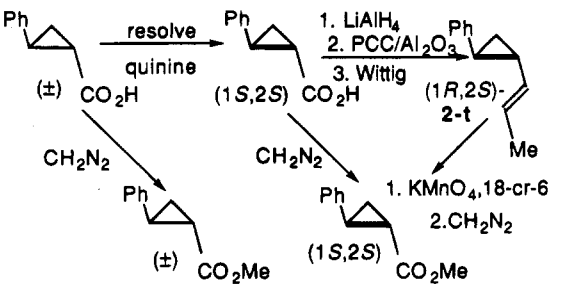
The time dependence of the concentration of the cis isomer is a function of the very same two exponentials. If [**2-c**] = 0 at $t = 0$, then $[\mathbf{2\text{-}c}, \%] = B_1(\exp(-\lambda_1 t) + B_2 \exp(-\lambda_2 t))$, with $B_1 = -B_2$; whatever the initial concentrations of **2-t** and **2-c**, the time dependence of both will depend on these two exponentials, with coefficients dependent on the initial concentrations.

The differential equations appropriate to the full set of reactions shown in Scheme 3, with stereomutations of the four 1-(*E*-1-propenyl)-2-phenylcyclopropanes taking

Scheme 3



Scheme 4



place along with the isomerizations to cyclopentenes, may also be solved exactly for the concentration differences [(1*R*,2*S*)-(1*S*,2*R*)-**2-t**] and [(1*S*,2*S*)-(1*R*,2*R*)-**2-c**] as functions of time.[13,14] Both differences depend on the same two exponential functions: thus $[(1R,2S)\text{-}(1S,2R)\text{-}\mathbf{2\text{-}t}] = C_1 \exp(-\eta_1 t) + C_2 \exp(-\eta_2 t)$ and $[(1S,2S)\text{-}(1R,2R)\text{-}\mathbf{2\text{-}c}] = D_1 \exp(-\eta_1 t) + D_2 \exp(-\eta_2 t)$, with the coefficients C_1, C_2, D_1, D_2 dependent on initial concentrations and ee values.

The weighted average ee over a given reaction time for **2-t**, $P(t)$, may be calculated by using the expressions given in eqs 3[6-8] and 4. Once the weighted average ee value for **2-t** for a given reaction time is determined, the relative rate constants k_{si}, k_{ar}, k_{sr}, and k_{ai} for isomerizations of **2-t** may be calculated from the concentration versus time data observed for its four 3-methyl-4-phenylcyclopentene vinylcyclopropane rearrangement products.

$$P(t) = \int_0^t (\text{ee of } [\mathbf{2\text{-}t}]) * ([\mathbf{2\text{-}t}])dt / \int_0^t ([\mathbf{2\text{-}t}])dt \quad (3)$$

$$P(t) = 100\frac{\int_0^t (C_1 e^{-\eta_1 t} + C_2 e^{-\eta_2 t})dt}{\int_0^t (A_1 e^{-\lambda_1 t} + A_2 e^{-\lambda_2 t})dt} \quad (4)$$

Results and Discussion

Syntheses. The chiral substrate (1*R*,2*S*)-**2-t** was prepared through the short route outlined in Scheme 4. Racemic *trans*-2-phenylcyclopropanecarboxylic acid is commercially available, and it may be resolved through the quinine salt to afford acid of high ee and known absolute stereochemistry.[15] A sample of the (1*S*,2*S*) acid of $[\alpha]_D + 368°$ ($CHCl_3$) (lit.[15a] $[\alpha]_D^{14} + 381°$ ($CHCl_3$); lit.[15d] $[\alpha]_D + 350°$ ($CHCl_3$) for a d_2-version of this acid) was secured; the corresponding methyl ester was found to

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Table 1. Isomer Distributions from Thermal Isomerizations of *trans*-1-(*E*-1-Propenyl)-2-phenylcyclopropane at 234.4 °C

time (min)	2-t (%)	2-c (%)	3-t (%)	3-c (%)
1.5	90.0	9.5	0.3	0.2
4	83.9	14.9	0.8	0.5
9	79.2	17.7	2.0	1.1
14	77.2	17.9	3.2	1.8
19[a]	75.5	17.7	4.5	2.3
29[a]	72.8	17.0	6.7	3.6
119	52.4	12.3	23.2	12.1

[a] Racemic starting material; all other runs with (1*R*,2*S*)-2-t.

Table 2. Isomer Distributions from Thermal Isomerizations of *cis*-1-(*E*-1-Propenyl)-2-phenylcyclopropane at 234.4 °C

time (min)	2-t (%)	2-c[a] (%)	3-t (%)	3-c (%)
0.5	12.0	87.6	0.2	0.1
2	41.0	57.5	1.0	0.5
3.5	61.6	36.0	1.7	0.8
6.5	73.7	22.5	2.6	1.2
14	75.1	17.5	4.8	2.6

[a] Racemic starting material.

have an enantiomeric excess of 99.6% according to chiral gas chromatographic analyses on a Lipodex E column.[16]

A conventional three-step reaction sequence ($LiAlH_4$ reduction, oxidation of the primary alcohol intermediate with pyridinium chlorochromate on alumina,[17] and finally a Wittig reaction with ethylidenetriphenylphosphorane under Schlosser conditions[18]) gave the required (1*R*,2*S*)-**2-t** hydrocarbon along with some of the related *Z* olefin. The substrate was purified by preparative gas chromatography and checked for ee: oxidation with $KMnO_4$/18-crown-6 in benzene[19] gave the acid, and diazomethane then afforded the methyl ester. It had the same high ee as the ester prepared directly from the resolved acid. The same reaction sequence applied to racemic *trans*-2-phenylcyclopropanecarboxylic acid, but with a less stereochemically selective Wittig procedure, provided the sample of *rac*-**2-t** used in some of the kinetic experiments.

Thermal Isomerizations Followed by Gas Chromatography. Samples of (1*R*,2*S*)-**2-t**, *rac*-**2-t, and** *rac*-**2-c** were sealed under reduced pressure in carefully prepared Pyrex ampoules, heated in an oil bath maintained at 234.4 °C for selected reaction times, cooled, and analyzed by gas chromatography on two capillary columns. The sample sizes (up to 60 mg) and the capacity of each ampoule (65 mL) used resulted in all of the $C_{12}H_{14}$ material being in the gas phase at the temperature of the reaction. The GC analytical results are summarized in Tables 1 and 2.

When the data of Table 1 relating [**2-t**] to time are subjected to a computer-implemented least-squares fit to the theoretical function derived above one finds [**2-t**, %] $= 18.7 \exp(-7.29 \times 10^{-3}t) + 81.3 \exp(-6.18 \times 10^{-5}t)$.[20]

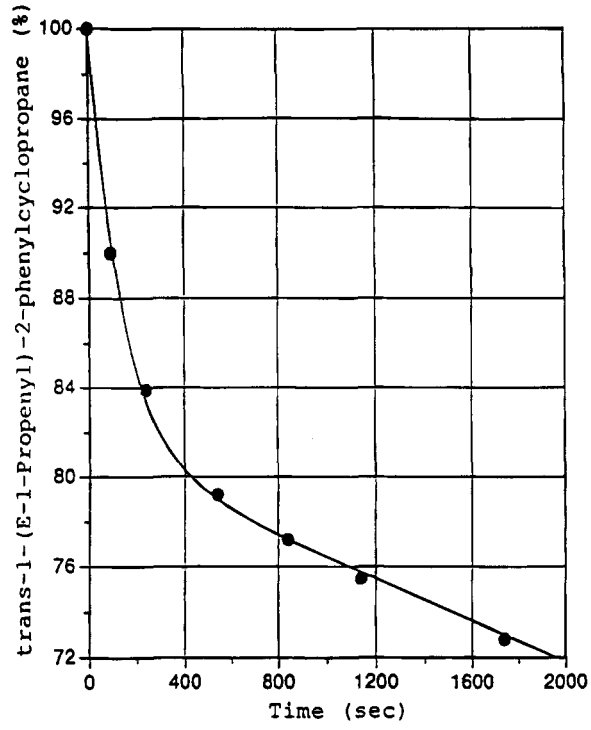

Figure 1. Concentration of **2-t** against time given by the data of Table 1 and the three-parameter equation [**2-t**, %] $= 18.7 \exp(-7.29 \times 10^{-3}t) + 81.3 \exp(-6.18 \times 10^{-5}t)$.

The graphical presentation of this theory-and-fit based function and the experimental points from 0 to 30 min are shown in Figure 1: the concentration of **2-t** falls very rapidly initially, as **2-c** is formed reversibly. When [**2-c**] data are treated in like fashion, the least-squares function found is [**2-c**, %] $= -18.9 \exp(-7.29 \times 10^{-3}t) + 18.9 \exp(-6.18 \times 10^{-5}t)$. This fit derives from optimization based on only one variable, since the exponential terms may be taken as constants. The quality of the fit shown in Figure 2 is quite comparable to the three-parameter fit displayed in Figure 1.

The concentrations [**2-t**] and [**2-c**] as functions of time (Table 2) also accord well with the expected two-exponential expressions: the best fits to the theoretical expressions give [**2-t**, %] $= -78.5 \exp(-7.29 \times 10^{-3}t) + 78.5 \exp(-6.18 \times 10^{-5}t)$ and [**2-c**, %] $= 80.3 \exp(-7.29 \times 10^{-3}t) + 19.7 \exp(-6.18 \times 10^{-5}t)$ (Figure 3). Each of these equations was calculated by fitting a single parameter, the exponential terms being taken as known constants.

The GC data thus define consistent integratable expressions for concentrations [**2-t**] and [**2-c**] as functions of time and provide an estimate for the equilibrium [**2-c**]/[**2-t**] ratio, about 0.23. At 234.4 °C, the half-life of the geometrical equilibration is about 95 s; the structural isomerization to cyclopentenes is much slower. The GC data provide one other valuable piece of information: the trans cyclopentene product **3-t** is 64% of the (**3-c** + **3-t**) mixture.

Weighted ee of *trans*-1-(*E*-1-Propenyl)-2-phenylcyclopropane. Samples of both cis and trans isomers of 1-(*E*-1-propenyl)-2-phenylcyclopropane recovered from the thermal reaction mixtures starting from (1*R*,2*S*)-**2-t** were isolated in pure form by preparative gas chromatography. The samples of **2-t** were oxidized with $KMnO_4$/

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(20) This and similar numerical calculations were done using DeltaGraph Pro 3 software (DeltaPoint, Inc., Monterey, CA 93940).

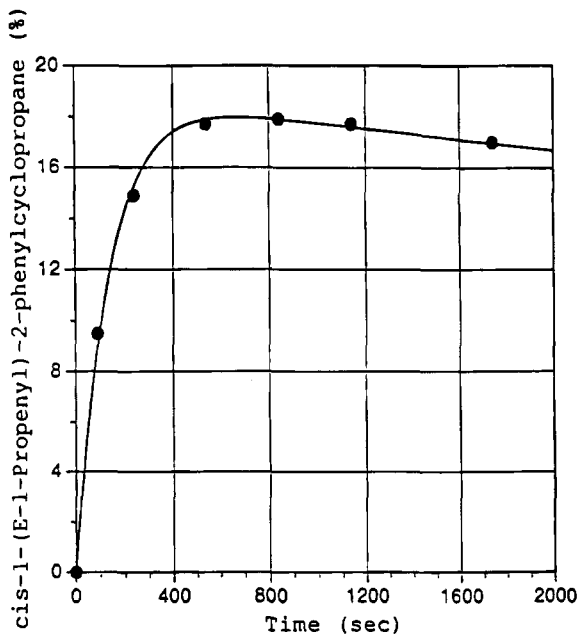


Figure 2. Concentration of **2-c** against time given by the data of Table 1 and the one-new-parameter equation [**2-c**, %] = $-18.9\exp(-7.29 \times 10^{-3}t) + 18.9\exp(-6.18 \times 10^{-5}t)$.

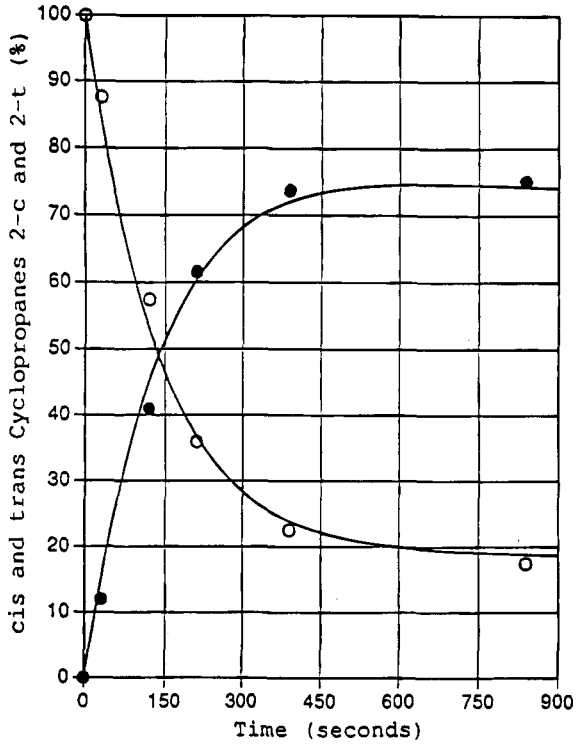


Figure 3. Time versus concentration for **2-t** and **2-c** based on the data of Table 2. The theoretical expressions for the one-variable-parameter functions plotted are given in the text.

18-crown-6 in benzene to give the corresponding *trans*-2-phenylcyclopropanecarboxylic acids; these acids were then esterified with diazomethane. The enantiomeric methyl *trans*-2-phenylcyclopropanecarboxylates were analyzed by chiral gas chromatography on the Lipodex E column.[16] Under the conditions employed, the separation of these enantiomers was excellent, the early eluting (1*R*,2*R*) isomer and the later eluting (1*S*,2*S*) isomer being separated by 3 min. Control experiments showed that the oxidation, esterification sequence does not lead to racemization. The ee values for **2-t** given in Table 3 are those measured for the corresponding mixtures of enantiomeric esters.

Table 3. Time Dependence of *trans*-1-(*E*-1-Propenyl)-2-phenylcyclopropane Enantiomeric Excess Values at 234.4 °C

time (min)	obsd[a] ee (%)	calcd[b] ee (%)	calcd[c] *P* (%)
0	100[d]	100	100
4	70	70.2	85.4
9	38	37.9	68.7
14	19	19.3	54.6
19		9.8	44.8

[a] By chiral GC analyses of derived methyl *trans*-2-phenylcyclopropanecarboxylates. [b] From ee (%) = $100\{179\exp(-2.52 \times 10^{-3}t) - 79\exp(-2.96 \times 10^{-3}t)\}/[\mathbf{2-t}]$. [c] Using the numerical parameters given in the text and exact solutions to eq 4. [d] 99.6% before rounding to nearest percent.

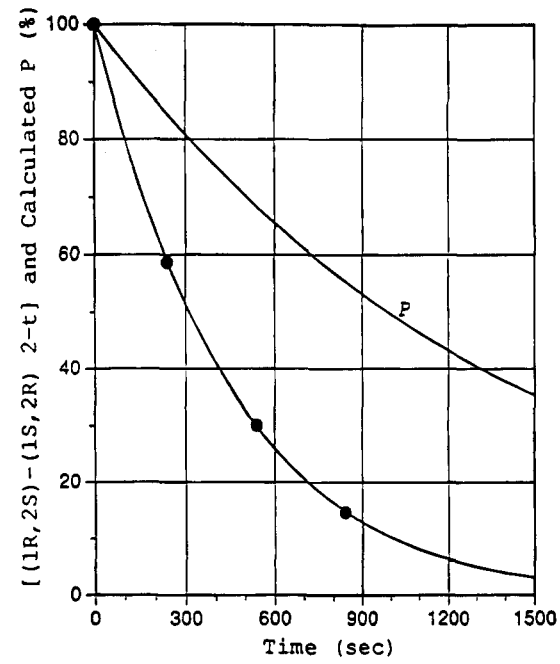


Figure 4. Experimental values for [(1*R*,2*S*)-(1*S*,2*R*)-**2-t**] derived from the data of Tables 1 and plots of [(1*R*,2*S*)-(1*S*,2*R*)-**2-t**] = $179\exp(-2.52 \times 10^{-3}t) - 79\exp(-2.96 \times 10^{-3}t)$ and of *P*(t), calculated with eq 4 and the necessary experimentally based parameters.

The time dependence of [(1*R*,2*S*)-(1*S*,2*R*)-**2-t**] was modeled using the appropriate function, [(1*R*,2*S*)-(1*S*,2*R*)-**2-t**] = $C_1\exp(-\eta_1 t) + C_2\exp(-\eta_2 t)$. The observed ee data summarized in Table 3 and the [**2-t**] data from Table 1 were used to calculate [(1*R*,2*S*)-(1*S*,2*R*)-**2-t**] values, and the best parameters for the theoretical function were found through an iterative least-squares calculation: [(1*R*,2*S*)-(1*S*,2*R*)-**2-t**] = $179\exp(-2.52 \times 10^{-3}t) - 79\exp(-2.96 \times 10^{-3}t)$. The parameters in this function are not known with great precision, since one cannot secure precise values for three parameters based on a fit to four experimental points, yet they do evidently give a good match to the experimental data, as one may see by considering the calculated ee values in Table 3 and the plot of Figure 4. The weighted ee values for **2-t** included in Table 3 were calculated using the appropriate formula (eq 4) and the necessary, experimentally based numerical parameters.

One should emphasize here an important qualitative point evident from the entries in Table 3: weighted ee values decrease more slowly than the enantiomeric excess

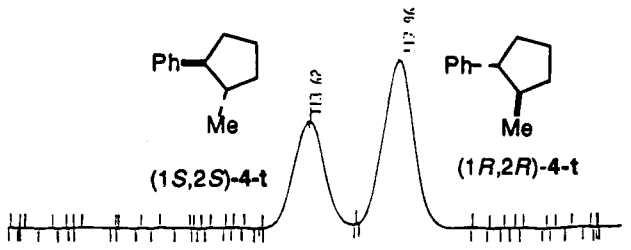


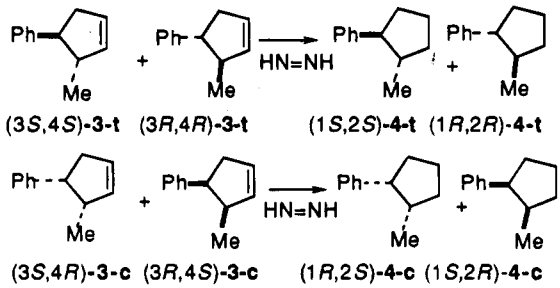
Figure 5. Chiral GC analysis of the cyclopentanes derived from **3-t** enantiomers formed from (1*R*,2*S*)-**2-t** in 9 min at 234.4 °C.

values for the reactant. After 19 min at 234.4 °C, the ee of the **2-t** reactant is calculated to be only 9.8%, but the weighted ee over the 19-min period is 44.8%. Product mixtures derived from **2-t** from a 19-min kinetic run might accordingly be treated as though they came from an invariant 72.4:27.6 ratio of enantiomers of the starting material.

Samples of **2-c** from the reactions of chiral **2-t** summarized in Table 1 were recovered and purified by preparative GC and then analyzed for ee directly on the Lipodex E column. They were found to be very nearly racemic: at t = 1.5, 4, 9, and 14 min the measured ee values were 4, 8, 3, and 3%. No effort was made to determine which enantiomer is formed slightly preferentially.

These ee data imply that the two one-center stereomutation rate constants for **2-t**, k_1 and k_2, are nearly identical and that the cyclopentenes which may be formed from the cis enantiomers of 1-(*E*-1-propenyl)-2-phenylcyclopropane will be essentially racemic, whatever the relative values of k_{si}' and k_{ar}', and of k_{sr}' versus k_{ai}'.

Separation, Assignment, and Quantitation of 3-t and 3-c Enantiomers. The isomeric products from the kinetic runs from (1*R*,2*S*)-**2-t** (Table 1) were collected by preparative gas chromatography on a Carbowax column and identified by spectroscopy. The cis and trans isomers **3-c** and **3-t** were separately reduced with diimide and the cis and trans isomers of 1-phenyl-2-methylcyclopentane obtained, **4-c** and **4-t**, were shown to be identical with authentic samples prepared by an independent route.[8]



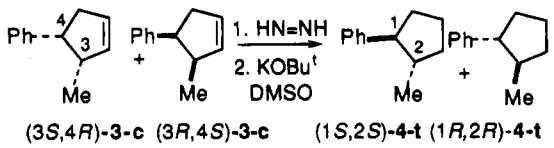
The trans isomers, (3*S*,4*S*)-**3-t** and (3*R*,4*R*)-**3-t**, corresponding to the ar and si products from (1*R*,2*S*)-**2-t**, were reduced with diimide, and the (1*S*,2*S*)-**4-t** and (1*R*,2*R*)-**4-t** mixture obtained was analyzed by chiral GC. In earlier work[8] it was established that these cyclopentanes separate well on a capillary Lipodex E chiral GC column and that (1*S*,2*S*)-**4-t** elutes before (1*R*,2*R*)-**4-t**. The analytical method is exemplified in Figure 5, showing the **4-t** enantiomers derived from the **3-t** enantiomers from the 9-min reaction. The major enantiomer is (1*R*,2*R*)-**4-t**, so the major enantiomer of the cyclopentene precursor is (3*R*,4*R*)-**3-t**, and the si path predominates over the ar alternative. Resolutions and quantitations of the **3-t** enantiomers from three product mixtures were completed; the results are summarized in Table 4.

Table 4. 3-Methyl-4-phenylcyclopentene Products from (1*R*,2*S*)-1-(*E*-1-Propenyl)-2-phenylcyclopropane at 234.4 °C

time (min)	(3*R*,4*R*)-**3-t** (si product)	(3*S*,4*S*)-**3-t** (ar product)	(3*R*,4*S*)-**3-c** (sr product)	(3*S*,4*R*)-**3-c** (ai product)
4	64.3[a]	35.7		
9	59.6	40.4	64.3[b]	35.7
14	58.2	41.8	59	41

[a] Percentage of total **3-t** that is (3*R*,4*R*). [b] Percentage of total **3-c** that is (3*R*,4*S*).

Quantitative analyses of the *cis*-3-methyl-4-phenylcyclopentene enantiomers were accomplished through a similar though less direct method; a mixture of (3*S*,4*R*)-**3-c** and (3*R*,4*S*)-**3-c** enantiomers from a kinetic run was isolated in pure form by preparative GC and reduced with diimide to the corresponding mixture of cis cyclopentanes. These cyclopentanes were then epimerized at the benzylic carbon with potassium *tert*-butoxide in dimethyl sulfoxide to give a mixture of (1*S*,2*S*)-**4-t** and (1*R*,2*R*)-**4-t** which could be analyzed by chiral GC.



Cis cyclopentene products from the 9-min and the 14-min kinetic runs were analyzed by this procedure; the dominant enantiomer formed was (3*R*,4*S*)-**3-c**, leading to (1*R*,2*R*)-**4-t** (Table 4), and thus the sr path for the vinylcyclopropane rearrangement is favored over the ai path.

3-Methyl-4-phenylcyclopentene Products from 2-c and 2-t. To learn how much of each cyclopentene product in reaction mixtures derived from isomerization of the **2-t** enantiomers, and how much from **2-c**, the **3-t** and **3-c** product distributions were plotted against reaction time and were fit with appropriate two-parameter equations. At any time t, $[\mathbf{3\text{-}c}] = a \int [\mathbf{2\text{-}c}]dt + b \int [\mathbf{2\text{-}t}]dt$, where $a = (k_{si}' + k_{ar}')$ and $b = (k_{sr} + k_{ai})$, and similarly $[\mathbf{3\text{-}t}] = c \int [\mathbf{2\text{-}c}]dt + d \int [\mathbf{2\text{-}t}]dt$, with $c = (k_{sr}' + k_{ai}')$ and $d = (k_{si} + k_{ar})$. Integratable expressions for the concentrations of [**2-c**] and [**2-t**] being available, the parameters a to d are readily obtained from the plots shown in Figure 6. The best parameters found through iterative least-squares calculations are a = 0.7, b = 2.4, c = 6.3, and d = 3.5 (all times 10^{-5} s^{-1}). Thus the k and k' rate constants of Scheme 2 are 5.9×10^{-5} s^{-1} and 7.0×10^{-5} s^{-1}, respectively. These rate constants and the ratios of time-interval-averages of [**2-t**]/[**2-c**] allow one to calculate the relative amounts of **3-t** and **3-c** formed from **2-t** and **2-c** at the times entered in Table 5. From λ_1 and λ_2 may be calculated[13] $k_i = 7.22 \times 10^{-3}$ s^{-1}, and $k_{tc} = 1.35 \times 10^{-3}$ s^{-1}.

The cyclopentenes stem predominantly from **2-t** enantiomers because (b or d) × [**2-t**] is always larger than (a or c) × [**2-c**]; the contribution of **2-c** to **3-c** is very close to negligible, but as much as a fourth of the **3-t** product comes from **2-c**.

Stereochemistry of the Rearrangement of (1*R*,2*S*)-2-t to 3-Methyl-4-phenylcyclopentenes. Some 64%

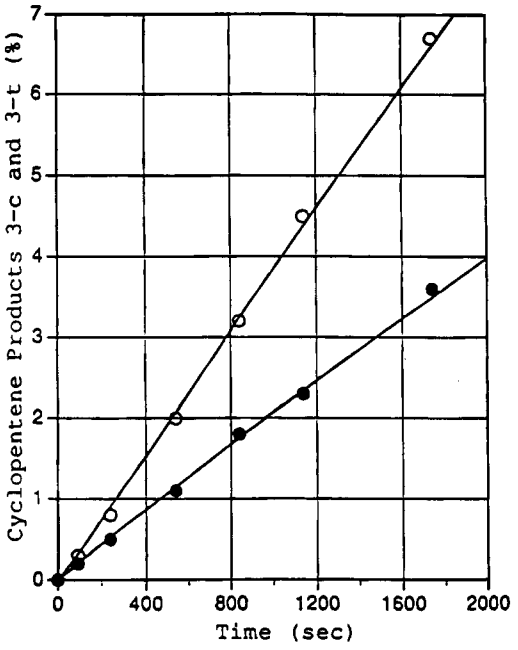


Figure 6. Plots of [**3-t**] (circles) and [**3-c**] (dots) in reactions mixtures from (1*R*,2*S*)-**2-t** (Table 1) against time; the theoretical plots are given by $[\mathbf{3\text{-}c}]10^5 = 0.7 \int [\mathbf{2\text{-}c}]dt + 2.4 \int [\mathbf{2\text{-}t}]dt$ and $[\mathbf{3\text{-}t}]10^5 = 6.3 \int [\mathbf{2\text{-}c}]dt + 3.5 \int [\mathbf{2\text{-}t}]dt$.

Table 5. Relative Amounts of 3-t and 3-c Formed From 2-t and 2-c at 234.4 °C in Mixtures Starting from (1*R*,2*S*)-2-t

time (min)	**2-t** → **3-t** (%)	**2-c** → **3-t** (%)	**2-t** → **3-c** (%)	**2-c** → **3-c** (%)
4	84	16	97	3.2
9	78	22	95	4.6
14	75	25	95	5.2

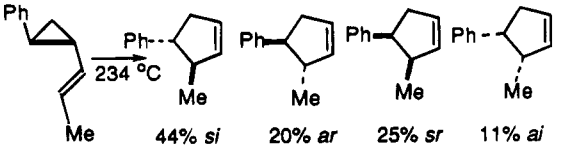
Table 6. Relative Magnitudes of the Four Rate Constants for (1*R*,2*S*)-1-(*E*-1-Propenyl)-2-phenylcyclopropane to 3-Methyl-4-phenylcyclopentenes at 234.4 °C

kinetic run (min)	k_{si} (%)	k_{ar} (%)	k_{sr} (%)	k_{ai} (%)
4	44.7	19.3	–	–
9	43.5	20.5	25.9	10.1
14	44.8	19.2	24.3	11.7

of the cyclopentene products are of trans stereochemistry (Table 1). From this fact, the weighted enantiomeric excess values for the reactant (1*R*,2*S*)-**2-t** listed in Table 3, the percentages of trans and of cis cyclopentene enantiomers given in Table 3, and the relative importance of **2-t** and **2-c** as direct progenators of **3-t** and **3-c** summarized in Table 5, one may deduce values of the relative magnitudes of the four rate constants k_{si}, k_{ar}, k_{sr}, and k_{ai} for vinylcyclopropane to cyclopentene isomerizations of **2-t**.

The calculations required are not complicated: for example, for the 4-min **3-t** products: $P(t) = 85.4\%$, or a 92.7:7.3 weighted average of (1*R*,2*S*)-**2-t** and (1*S*,2*R*)-**2-t** enantiomers. The enantiomers of **3-t** are formed in a 64.3%:35.7% ratio; 8% of each stems from **2-c**, so the ratio from **2-t** is 56.3:27.7, or 67:33 after normalization. Letting x be the fractional preference for the si mode over the ar mode, $92.7x + 7.3(1 - x) = 67$, or $x = 0.70$, and $64x = 44.7$, the figure entered in Table 6 for the percent participation of the si mode. The experimental uncertainties in these percentages summarized in Table 6 are considered to be on the order of 2%.

Scheme 5



The stereochemical results in Table 6, summarized in Scheme 5, do not seem very sensitive to changes in the concentration of **2-c** ranging from zero to 17.9% over the first 14 min of the thermal reactions; nor do they trend particularly as the ee of **2-t** reactant declines from 100 to 19%. The kinetic model employed serves well to allow for the dynamic nature of the mixture of starting materials and to ascertain the relative magnitudes of k_{si}, k_{ar}, k_{sr}, and k_{ai}.

If one were to neglect the contributions of reactions giving **3-t** and **3-c** directly from the enantiomers of **2-c**, the calculated relative importances of the k_{si}, k_{ar}, k_{sr}, and k_{ai} rate constants would have been 42, 22, 25, and 11%—not a very different pattern. The stereochemical results are simply not very sensitive to the contributions to product mixtures from **2-c** since the contributions are limited and because **2-c** derived thermally from chiral **2-t** is very nearly racemic.

Discussion

Other Stereochemical Results. Work with different systems has provided additional information relevant to the stereochemistry and mechanism of rearrangements of vinylcyclopropanes to cyclopentenes. (−)-*trans*-1-Isopropenyl-2-cyanocyclopropane is converted thermally to 1-methyl-4-cyanocyclopentene with 70% inversion at the migrating carbon atom.[21] (+)-*trans*-1-(1-*tert*-Butylethenyl)-2-methylcyclopropane rearranges to 1-(*tert*-butyl)-4-methylcyclopentene with 85% inversion at the migrating carbon; racemic *trans*-1-(1-*tert*-butyl-2-*Z*-deuterioethenyl)-2-methylcyclopropane provides 1-(*tert*-butyl)-4-methyl-5-deuteriocyclopentenes indicative of some 86% of the rearrangement taking place through allowed si and ar paths.[22,23] An appropriately labeled 1-(*tert*-butylethenyl)cyclopropane-d_3 was thermally isomerized to 1-(*tert*-butyl)-3,4,5-d_3-cyclopentenes with a high stereospecificity, apparently in excess of 85%, favoring the si path.[24] Thus the consistent stereochemical preference for isomerization of *trans*-1-alkenyl-2-deuterio(or cyano or methyl or phenyl)cyclopropanes with net inversion at the migration carbon is not driven by steric repulsion or some thermodynamic bias. Migration with inversion is favored by smaller, rather than by larger, substituents at C2.

Relative Magnitudes of Rates Constants for Stereomutations and Rearrangements. Rearrangements of vinylcyclopropanes to cyclopentenes are consistently slower than the simultaneous enantiomerizations and geometrical isomerizations they exhibit; typical k_{12}/k ratios, for example, are about 6–7, corresponding to $\Delta\Delta G^{\ddagger}$ values of about 2 kcal/mol, while k_{tr}/k_{12} ratios are usually 2 to 3.[6-8] The theoretical expression found above for

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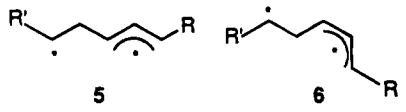
[(1*R*,2*S*)-(1*S*,2*R*)-**2-t**] as a function of time allows one to estimate k_{12}, the rate constant for enantiomerization of (1*R*,2*S*)-**2-t** to (1*S*,2*R*)-**2-t**, or vice versa. One may calculate the time derivative of [(1*R*,2*S*)-(1*S*,2*R*)-**2-t**] and evaluate it at $t = 0$; the value obtained, -2.17×10^{-3} s^{-1}, is equal to $-(2k_{12} + k_{tc} + k)$. Since $k = k_{si} + k_{ar} + k_{sr} + k_{ai} = 5.9 \times 10^{-5}$ s^{-1}, and $k_{tc} = 1.35 \times 10^{-3}$ s^{-1}, k_{12} is estimated to be 3.8×10^{-4} s^{-1}. This value of k_{12} is qualitatively in line with expectations, for $k_{12}/k \approx 6.4$, and $k_{tc}/k_{12} \approx 3.6$.

Substituents better able to stabilize diradical transition structures favor both enantiomerization and vinylcyclopropane-to-cyclopentene reactions, but only in enantiomerization and other stereomutation reactions is the full radical-stabilizing potential of the 1-alkenyl group apparent at the transition state. It may not be developed, or it may be present, but offset by a relatively invariant destabilizing steric effect. Stereomutation reactions may take place through diradical transition structures having the alkenyl function disposed in an extended form (**5**), but diradicals able to form cyclopentene products must have the allyl moiety fixed so that a *cis*-cyclopentene may be generated (**6**). The steric strain present in **6** could well be a factor. The conformational difference between **5** and **6** is reminiscent of that between the *E* and *Z* isomers of the butenyl cation, estimated to be about 1.6 kcal/mol favoring the *E* form.[25]



5 **6**

Secondary Deuterium Kinetic Isotope Effects provide additional information of mechanistic significance. Through kinetic work with vinylcyclopropane and its 2,2-d_2 and 2′,2′-d_2 analogs, Chickos found substantial normal effects, $k_H/k_D = 1.14$ and 1.17 at 338 °C.[26] Kinetic studies on *trans*-1-vinyl-2-methylcyclopropane and *trans*-1-(1-*tert*-butylethenyl)-2-(d_3-methyl)-cyclopropane, and the corresponding systems having deuterium in place of both hydrogens at the migration termini, found k_H/k_D values of 1.13 and 1.17 at 280 °C.[23] The implication drawn was that there is torsional distortion at the migration terminus in the transition structures, or at least in the kinetically most significant transition structures, and thus bond making in the rate-determining step(s); yet there is neither the significant energy of concert nor the high stereoselectivity normally seen in reactions generally supposed to be orbitally symmetry allowed and concerted! This puzzling dichotomy, and mechanistic parallels between vinylcyclopropane rearrangements and the stereomutation reactions of cyclopropanes,[27] still await full explications.

Conclusions

The vinylcyclopropane-to-cyclopentene thermal rearrangement of (1*R*,2*S*)-1-(*E*-1-propenyl)-2-phenylcyclopropane occurs through four stereochemically distinct reactions: the relative rate constants found at 234.4 °C are 44% si, 20% ar, 25% sr, and 11% ai. Thus the rearrangement is not subject to the strictures of orbital symmetry control; the "allowed" products have no important kinetic advantage over "forbidden" products, and no substantial energy of concert is associated with the si and ar reaction modes.

To secure this first complete delineation of stereochemistry for the rearrangement of a vinylcyclopropane system not having a methyl substituent at C2, much faster geometric isomerization and racemization reactions had to be dealt with: concentration and enantiomeric excess of the reactant as functions of time had to be determined experimentally and accurate stereochemical definitions of cyclopentene product mixtures had to be secured at quite low (up to a few percent) conversions to cyclopentenes. That the experimental and analytical tactics employed proved successful bodes well for similar approaches to other rearrangements where stereochemical information on a relatively slow reaction is hard to gain because concomitant reactions compromise the stereochemical integrity of a reactant much faster than substantial amounts of stereochemically informative products are formed.

The new stereochemical result summarized in Scheme 5 and the relative rate constants for the four paths followed in rearrangements shown by three *trans*-1-alkenyl-2-methylcyclopropanes listed in Scheme 1 demonstrate that the stereochemical course of these [1,3] carbon shifts is but little influenced by the nature of substituents disposed *E* on the ethenyl group and trans at C2; the C2 phenyl in the present work speeds bond breaking relative to C2 methyl systems, a facilitation evident in both stereomutations and in the rearrangement, but it does not dramatically alter the relative rate constants of the four paths to cyclopentene products. Whether these paths for a given vinylcyclopropane should be viewed as four geometrically distinct trajectories through configuration space, which happen to have nearly identical transition state energies, or paths branching from a common short-lived intermediate, remains to be discovered.

Stereochemical information on the rearrangement of isotopically labeled versions of vinylcyclopropane itself, and on other substituted systems that may exhibit stereochemical patterns fundamentally different from those seen to date, may contribute toward that discovery and are being sought. Theoretical efforts to define the potential energy surface for the rearrangement face substantial methodological challenges, but serious efforts are underway[28,29] and should in time provide telling insights. One may hope that experimental stereochemical results for diverse systems, and fundamental theory, will be mutually illuminating.

Experimental Section

Preparative gas chromatography was performed on a Varian Aerograph A90-P3 using a 1-m × 4.8-mm i.d. 20% Carbowax 20 M aluminum column and helium as carrier gas. Analytical GC was conducted two-dimensionally on a Hewlett-Packard (HP) 5790 gas chromatograph equipped with one injection port, two flame ionization detectors, HP crosslinked methyl silicone and 5% phenyl methyl silicone 25-m x 2-mm 0.33 μm ultra-

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performance capillary columns, and a dual channel HP 3396 Series 2 reporting integrator, with helium as carrier gas. Chiral GC analyses were done isothermally using a 50-m 0.25 mm i.d. 0.4 mm o.d. fused silica Lipodex E column, with octakis(2,6-di-*O*-pentyl-3-*O*-butyryl)-γ-cyclodextrin as the stationary phase (Machery-Nagel, Düren, Germany).

Mass spectra were determined with a HP 5970 mass selective detector interfaced with a HP 5890 gas chromatograph using a HP 25-m × 2-mm 0.33 μm ultra-performance crosslinked methyl silicone column and a HP 59970B workstation. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ solutions on a General Electric QE-300 spectrometer. Chemical shifts are reported in ppm relative to Me_4Si at 0.0 ppm. Optical rotations were measured on a Perkin-Elmer 241 polarimeter at 589 (Na) nm, using a 1-mL 100-mm path-length glass microcell. Microanalyses were performed by E + R Microanalytical Laboratories, Inc., Corona, NY.

***trans*-2-Phenylcyclopropanemethanol**[30] was prepared through the reduction of *trans*-2-phenylcyclopropanecarboxylic acid (Aldrich) with $LiAlH_4$ in ether.

***trans*-1-(*E*-1-propenyl)-2-phenylcyclopropane (*rac*-2-t).** *trans*-2-Phenylcyclopropanemethanol (1.78 g, 12 mmol) dissolved in 50 mL of dry hexane was placed in a round-bottomed flask, and 36.2 g of PCC on alumina (33 mmol of PCC) was added with stirring.[16] The reaction mixture was stirred for 3.5 h then filtered through a sintered glass funnel containing a 1:1 mixture of Celite and Florisil. The salts were washed with 300 mL of anhydrous ether and the filtrate was dried over 3A molecular sieves. In a separate flask, ethylidenetriphenylphosphorane was prepared from 7.43 g (20 mmol) of (ethyl)triphenylphosphonium bromide dissolved in 40 mL of dry ether and 15.4 mL of 1.3 M *sec*-butyllithium in hexane at 0 °C in the presence of 3A molecular sieves.[19] To the cooled reaction mixture was added the ethereal solution of *trans*-2-phenylcyclopropanecarboxaldehyde; the reaction mixture was allowed to warm to room temperature and was stirred for 18 h. Filtration through a sintered glass funnel containing Celite gave a filtrate which was washed repeatedly with distilled water, dilute aqueous HCl, and brine and was dried over Na_2SO_4. Filtration and concentration of the ethereal filtrate afforded 843 mg (45%) of a mixture of *E* and *Z* olefins in a 1:2.1 ratio, respectively. A sample of the *E* olefin was purified by preparative GC for characterization: MS *m/e* (%) 158 (M^+, 25), 143 (45), 129 (100), 128 (67), 115 (32), 91 (26), 39 (22); ^1H NMR: δ 1.06 (m, 1H), 1.17 (m, 1H), 1.61 (m, 1H), 1.67 (d, J = 6.4 Hz, 3H), 1.84 (m, 1H), 5.17 (dd, J = 8.2, 15 Hz, 1H), 5.53 (m, 1H), 7.15 (m, 5H); ^{13}C NMR: δ 16.5, 17.8, 24.8, 26.4, 123.7, 125.4, 125.6, 128.3, 133.2, 140.6. Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.99; H, 8.80.

For the *Z* olefin: MS *m/e* (%) 158 (M^+, 23), 143 (43), 129 (100), 128 (64), 115 (32), 91 (26), 39 (22); ^1H NMR: δ 1.08 (m, 1H), 1.23 (m, 1H), 1.71 (dd, J = 1.6, 6.9 Hz, 3H), 1.83 (m, 2H), 4.96 (doublet of triplets, J = 1.5, 9.8, 1H), 5.43 (m, 1H), 7.18 (m, 5H); ^{13}C NMR: δ 13.3, 17.2, 22.4, 25.1, 123.2, 125.5, 125.7, 128.3, 133.0, 140.1.

(1*R*,2*S*)-1-(*E*-1-propenyl)-2-phenylcyclopropane ((1R,2S)-2-t)) was prepared from 500 mg (3.08 mmol) of (1*S*,2*S*)-2-phenylcyclopropanecarboxylic acid,[15] $[\alpha]_D$ +368° (*c* = 1.3, $CHCl_3$); 99.6% ee by GC analysis of the related methyl ester on the Lipodex E column. Reduction and oxidation as described above for racemic material gave (1*S*,2*S*)-2-phenylcyclopropanecarboxaldehyde. Ethylidenetriphenylphosphorane was prepared by reacting 1.49 g (4 mmol) of (ethyl)triphenylphosphonium bromide in 25 mL of anhydrous THF in the presence of 3A molecular sieves at −78 °C with 1 equiv (2 mL) of 2.0 M butyllithium in cyclohexane.[17] The deep red solution was warmed briefly to 0 °C and then cooled again to −78 °C. The (1*S*,2*S*) aldehyde was then added to the stirred solution of Wittig reagent and the reaction mixture was stirred for 45 min. A second equivalent of butyllithium in cyclohexane was added to the reaction mixture at −78 °C; it was maintained at that temperature with stirring for 45 min and then 0.375 mL of *tert*-butyl alcohol (4 mmol) was added dropwise. The cold bath was removed and the contents of the reaction flask were allowed to warm to room temperature and were stirred overnight. After workup and distillation, 375 mg (77% from (1*S*,2*S*)-2-phenylcyclopropanemethanol) of (1*R*,2*S*)-**2-t** and the related *Z* isomer was obtained; the *E*:*Z* olefin ratio from the Wittig reaction was 3.7:1. Preparative GC gave the (1*R*,2*S*)-**2-t** sample, a 91.6:8.4% *E*:*Z* olefin mixture, used for kinetic experiments.

Thermal Reactions of 1-(*E*-1-propenyl)-2-phenylcyclopropanes were run using sealed ampoules and a constant temperature bath. Each 65-mL cylindrical Pyrex bulb was fitted with a 6-mm Pyrex tubing stem about 20 cm in length. The bulbs were soaked in concd HCl for at least 24 h, rinsed with water, soaked in concd NH_4OH saturated with EDTA for 48 h, and then rinsed at least 20 times with distilled water and dried for 1 wk at 160 °C.

The sample of *rac*-**2-t** utilized in the 19 and 29 min thermal reactions was purified by prep GC; it was a 99:1 mixture of *E*:*Z* isomers. Approximately 50 to 60 mg of (1*R*,2*S*)-**2-t** or *rac*-**2-t** was placed in each reaction bulb for the 4, 9, 14, and 119 min runs with the aid of a microsyringe. Smaller samples sizes, 10 mg or less, were utilized for the 1.5, 19 and 29 min pyrolyses, and for the kinetic runs starting with preparative GC purified *rac*-**2-c**, recovered from various thermal reaction mixtures. All reactions were run neat. Each bulb containing a sample was subjected to two freeze-pump-thaw cycles. Finally the bulbs were sealed under vacuum at −78 °C. The individual reaction bulbs were completely submerged in an oil bath regulated by a Bayley 253 temperature controller to a temperature of (234.4 ± 0.2) °C for a given time; the t = 0 reaction time was taken to be 1 min after the bulb was submerged in the bath. The bath oil, polyphenylsiloxane, was stirred by a Lightnin mechanical stirrer and temperature was monitored by a calibrated digital platinum resistance thermometer (HP-2802A, with HP-3474A display). After a reaction, the bulb was removed and cooled to room temperature. The stem of the bulb was scored; the bulb was cooled briefly in a dry ice/acetone bath and then opened.

Analyses of product mixtures were done by analytical GC using a temperature program starting at 100 °C and increasing at 5 °C/min. The values reported in Table 1 have been normalized to exclude the initially present *trans*-1-(*Z*-1-propenyl)-2-phenylcyclopropane and its rearrangement product, *cis*-1-(*Z*-1-propenyl)-2-phenylcyclopropane, which amounts to about 18% of the *Z*-propenyl compounds at equilibrium.[31] Both *Z*-propenyl compounds were well separated from all isomers included in Table 1 in analytical and preparative GC separations. There were neither visual nor GC indications of decompositions or other thermal reactions accompanying the isomerizations being investigated.

The products of thermolysis were separated from one another by preparative GC. The three products were identified by their spectral characteristics as the *cis* and *trans* isomers of 3-methyl-4-phenylcyclopentene and the cis isomer of the starting material. For the *trans* isomer **3-t**: MS *m/e* (%) 158 (M^+, 61), 143 (63), 129 (100), 128 (66), 115 (36), 91 (23), 77 (15), 39 (18); ^1H NMR: δ 1.08 (d, J = 6.3 Hz, 3H), 2.48 (m, 1H), 2.83 (m, 3H), 5.66 (m, 1H), 5.73 (m, 1H), 7.27 (m, 5H); ^{13}C NMR: δ 20, 41.8, 48.9, 53.2, 125.9, 127.4, 128.3, 128.5, 136, 148.5. Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.06; H, 8.80.

For the *cis* isomer **3-c**: MS *m/e* (%) 158 (M^+, 55), 143 (55), 129 (100), 128 (62), 115 (36), 91 (22), 77 (15), 39 (18); ^1H NMR: δ 0.58 (d, J = 7.1 Hz, 3H), 2.66 (m, 2H), 2.97 (broad t, J = 7.2 Hz, 1H), 3.55 (q, J = 8.3 Hz, 1H), 5.77 (m, 1H), 5.82 (m, 1H), 7.24 (m, 5H); ^{13}C NMR: δ 15.8, 31.8, 36.4, 47.5, 125.8, 127.9, 128.4, 129.1, 136.8, 148.5 ppm.

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For the third product, *cis*-1-(*E*-1-propenyl)-2-phenylcyclopropane, **2-c**: MS *m/e* (%) 158 (M^+, 31), 143 (49), 129 (100), 128 (72), 115 (37), 91 (28), 77 (21), 51 (18), 39 (21); ^{1}H NMR: δ 0.94 (q, J = 5.7 Hz, 1H), 1.21 (m, 1H), 1.54 (dd, J = 1.5, 6.4 Hz, 3H), 1.81 (m, 1H), 2.26 (q, J = 8.6 Hz, 1H), 4.78 (ddd, J = 1.5, 9, 15.2 Hz, 1H), 5.56 (m, 1H), 7.24 (m, 5H); ^{13}C NMR δ 11.5, 18, 22, 22.8, 125.2, 125.7, 127.9, 129, 130, 139.2.

The recovered samples of partially racemized (1*R*,2*S*)-**2-t** were subjected to oxidation by $KMnO_4$ in benzene containing the crown ether 18-C-6.[18] The methyl 2-phenylcyclopropanecarboxylates from treatment of the acids with diazomethane were analyzed by chiral GC isothermally at 95 °C. The ee data for these methyl esters are summarized in Table 2.

Samples of **2-c** isolated from four reaction mixtures starting from (1*R*,2*S*)-**2-t** were analyzed directly for ee on the Lipodex E column at 65 °C, conditions which separate the two enantiomers cleanly, by 4.5 min. The kinetic samples proved to be nearly racemic, the later eluting enantiomer being in slight excess. After reaction times of 1.5, 4, 9, and 14 min, the measured ee values of the recovered **2-c** samples were 4, 8, 3, and 3%.

The *trans* and *cis* isomers of **3** were separated completely by prep GC and were separately reduced with diimide[32] to give the *trans* and *cis* isomers of 1-phenyl-2-methylcyclopentane. Direct comparisons with authentic samples of these hydrocarbons[8] confirmed the structural assignments. The enantiomeric forms of **4-t** may be readily distinguished by chiral GC; on the Lipodex E column, the (1*S*,2*S*)-**4-t** enantiomer elutes before the (1*R*,2*R*)-**4-t** enantiomer.[8] Such analyses of the enantiomers of *trans*-1-phenyl-2-methylcyclopentane derived from thermal rearrangement products **3-t** through diimide reductions are reported in Table 3.

Samples of **4-c** were epimerized at the benzylic carbon with potassium *tert*-butoxide in DMSO at 80 °C for 3 h[33] to yield chiral GC separable *trans* isomers having the same absolute stereochemistry at C2 of **4-t** as was present at C3 of the rearrangement product **3-c**. Chiral GC analyses of these *trans*-1-phenyl-2-methylcyclopentanes are given in Table 3.

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