the Advancement of Pure Research (ZWO).

Registry No. 1, 31886-99-4; 2, 80206-71-9; 3, 80206-70-8; *endo*-4, 81045-21-8; *exo*-4, 81129-81-9; 5, 86803-55-6; 6, 86803-56-7; 10, 86803-57-8; 11, 86803-58-9; 12, 86803-59-0; 13, 86803-60-3; 14, 86803-61-4; 15, 86803-62-5; 15($AlCl_3$), 86822-05-1; 17, 86803-63-6; 17($AlCl_3$), 86834-24-4; 18, 86803-64-7; 19, 86803-65-8; $AlCl_3$, 7446-70-0; $AlBr_3$, 7727-15-3; *N*-phenyl-2,3,4,5-tetramethylpyrrole, 1015-63-0; *N*-(*p*-chlorophenyl)-2,3,4,5-tetramethylpyrrole, 86803-66-9; *N*-(*p*-methoxyphenyl)-2,3,4,5-tetramethylpyrrole, 86803-67-0; *N*-*p*-tolyl-2,3,4,5-tetramethylpyrrole, 86803-68-1; PhN=S=O, 1122-83-4; *p*-ClPhN=S=O, 13165-68-9; *p*-(CH_3O)PhN=S=O, 13165-69-0; *p*-(CH_3)PhN=S=O, 15795-42-3; 2-butyne, 503-17-3; propyne, 74-99-7; *endo*-4,5-(4-methylbenzo)-1,6,7,8-tetramethyl-2-thia-3-azabicyclo[4.2.0]oct-7-ene 2-oxide, 86803-69-2; *endo*-4,5-(4-methylbenzo)-6,8-dimethyl-2-thia-3-azabicyclo[4.2.0]oct-7-ene 2-oxide, 86803-70-5; *endo*-4,5-(4-methoxybenzo)-1,6,7,8-tetramethyl-2-thia-3-azabicyclo-[4.2.0]oct-7-ene 2-oxide, 86803-71-6; *endo*-4,5-(4-chlorobenzo)-1,6,7,8-tetramethyl-2-thia-3-azabicyclo[4.2.0]oct-7-ene 2-oxide, 86803-72-7; *exo*-4,5-(4-chlorobenzo)-1,6,7,8-tetramethyl-2-thia-3-azabicyclo[4.2.0]oct-7-ene 2-oxide, 86851-44-7; 4,5-(4-chlorobenzo)-1,6,7,8-tetramethyl-2-thia-3-azabicicylo[4.2.0]oct-7-ene 2,2-dioxide, 86803-73-8; *N*-(2,6-dimethylphenyl)sulfinylamine, 17420-02-9; *N*-*tert*-butylsulfinylamine, 38662-39-4; *N*-(*p*-nitrophenyl)-2,3,4,5-tetramethylpyrrole, 86803-74-9.

Steric Retard of Internal Rotation in 1-Carbomethoxy-1,2-diphenylcyclopropane

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The high preference (R_A = 13) found by Chmurny and Cram for internal rotation of the hydrogen–phenyl carbon bond over the carbomethoxy–phenyl carbon bond in 1-carbomethoxy-1,2-diphenylcyclopropane appears to originate in a steric effect. There being nothing out of the ordinary in 1-carbomethoxy-2-phenylcyclopropane (R_A = 1.7) vis-à-vis 1-cyano-2-phenylcyclopropane (R_A = 2.5), the ester group of itself is probably not at fault. When it is replaced by cyano in 1-cyano-1,2-diphenylcyclopropane, R_A drops dramatically to 2.2. This marked increase in rotational propensity of the cyano–phenyl carbon bond vis-à-vis the carbomethoxy–phenyl carbon bond is reasonably ascribed to the smaller steric thickness of the cyano group and a reduced steric hindrance to rotation past the hydrogen–phenyl carbon bond.

Internal rotational propensity is the key to automerization in substituted cyclopropanes[1] and cyclobutanes.[2] If the activation energies of the hypothetical reactions are accommodated by a simple model consisting of the appropriate carbon–carbon bond dissociation energy[3] decreased by full release of ring strain and by radical-stabilizing effects of any substituents on the several bonds, the stereochemistry of the products is determined by the ratio of single to double rotations and, within the set of single rotations, by the preference of one disubstituted carbon atom to rotate over another (Figure 1). This preference, the relative internal rotational propensity, is a thermodynamic quantity[1] defined (see Figure 1) as

$$R_A = R_{YZ}^{AB} = k_{TC(AB)}/k_{TC(YZ)} = k_{CT(AB)}/k_{CT(YZ)} = k_1/k_2 = k_{-1}/k_{-2}$$

Except for an example of Chmurny and Cram,[4] which provides the stimulus for the present work, magnitudes of known rotational preferences given in Table I are neither impressively large nor clearly revealing of controlling factors. A complicated 1,2,3-trisubstituted example has been omitted but indicates a significant steric influence on R_A by the substituent at C_3.[7]

Whatever effect replacement of a shorter, smaller group by a longer, larger group might have been expected to have (cf. ref 3 and 5, Table I), the effect is small and opposite to that anticipated from a change in moments of inertia. Similarly, an approximate doubling in molecular weight (cf. 1 or 2 and 3, or 4 and 6, Table I) has no significant influence on the value of R_A.

Uniquely dramatic among this collection is the relative rotational propensity calculable from the experimental results of Chmurny and Cram[4] (Figure 2, **2t** and **2c**) on 1-carbomethoxy-1,2-diphenylcyclopropane. Its exceptionally high value (R_A = 13.3) begged for an explanation, which, it might be hoped, would give insight into the origins of rotational propensity. The present experiments were designed to determine whether an ester group might be peculiar by itself or whether the special environment of the Chmurny–Cram example might be responsible. Replacement of the ester group by the sterically narrower cyano group offered promise of useful information.

Results

Methyl 1,2-Diphenylcyclopropanecarboxylate. The starting point is the mixture of **1t** and **1c** prepared following Chmurny and Cram with minor modifications.[4] Convenient separation is effected either by crystallization or by partial saponification of the methyl esters, wherein **2c** hydrolyzes about 8 times faster than **2t**. This observation is fully consistent with the configurational assignments of Chmurny and Cram, which are based on an upfield shift in the NMR spectrum of the methyl group in **2t**, comparison of the pK_a values of **1t** and **1c** with those

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Table I. Internal Rotational Preference of C_{AB} over C_{YZ} in Automerization of Cyclopropanes (Refer to Figure 1)

	A	B	Y	Z	R_{XY}^{AB}	$K_{t/c}$	T, °C	ref
1	CN	H	CH=CHCH$_3$(*E*)	H	2.36	1.47	207.1	*a*
2	CN	H	C(CH$_3$)=CH$_2$	H	2.20	2.67	217.8	1
3	CN	H	C_6H_5	H	2.47	2.79	217.8	5
4	C(CH$_3$)=CH$_2$	H	C_6H_5	H	1.26	10.11	169.5	5
5	CN	H	C≡CC$_6$H$_5$	H	1.76	1.66	190.7	5
6	CH$_3$	H	CH$_2$CH$_3$	H	1.17	2.86	404.3	*b*
7	CN	H	CN	H	1.00	2.83	259.5	6
8	CN	H	CN	CH$_3$	1.4	2.27	259.5	6
9	C_6H_5	H	C_6H_5	COOCH$_3$	18.0	0.47	192.6	this work
10	C_6H_5	H	C_6H_5	CN	2.15	3.25	146.0	this work
11	COOCH$_3$	H	C_6H_5	H	1.69	10.8	258.1	this work

[a] Quoted in ref 2 from: Barsa, E. A., Ph.D. Dissertation, Harvard University, Cambridge, MA 1976. [b] Carter, W. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1968**, *90*, 7344-7346. Bergman, R. G.; Carter, W. L. *Ibid.* **1969**, *91*, 7411-7425.

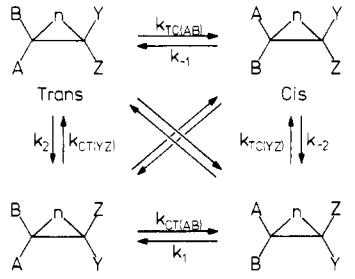
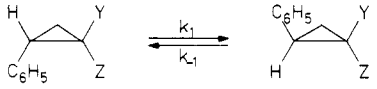


Figure 1. Single and double internal rotations in 1,2-substituted cyclopropanes (n = one CH_2 group) and cyclobutanes (n = two CH_2 groups).



k_1	k_{-1}		Y	Z		T°C	Table
		1t	C_6H_5	COOH	1c		
2.29	1.08	2t	C_6H_5	COOCH$_3$	2c	192.6	II
2.47	8.03	3t	C_6H_5	CN	3c	145.7	V
		4t	C_6H_5	COCH$_3$	4c		
		5t	COOH	H	5c		
0.11	1.14	6t	COOCH$_3$	H	6c	255.0	IV
		7t	CN	H	7c		

Figure 2. The set of di- and trisubstituted derivatives of cyclopropane comprising the substrates of this work. "Trans" (t) and "cis" (c) designate the stereochemical relation between the phenyl group of the hydrogen–phenyl carbon and the Y group of the Y–Z carbon atom. Values of k_1 and k_{-1} are in units of 10^{-5} s^{-1}. For values of $K_{t/c}$ and R_A, see Table I.

of (*Z*)- and (*E*)-α-phenylcinnamic acids, and comparison of the equilibrium constant between **2t** and **2c** and that between the two α-phenylcinnamic acids. Likewise consistent with their assignment is the change in position of equilibrium (**2c**/**2t**) from 2.11 in the ester to 0.313 in the nitrile (**3c**/**3t**).

The carboxylic acid, **1t**, is resolved via its quinine salt[8] whereas **1c** is resolved as its ephedrine salt. Optical purity is determined directly by NMR on the basis of separations induced by chiral lanthanide reagents. Chmurny and Cram have already shown by ozonolysis to cyclopropane-1,1,2-tricarboxylic acid that (−)-**2t** and (+)-**2c** are epimeric at C_2, the hydrogen–phenyl carbon.

The rate of the thermal interconversion of **2t** and **2c** in dilute solution in benzene is determined at 192.6 ± 0.3 °C. Analysis is effected by capillary GLC. No difference between ampules made of Pyrex and lead–potash being observed, acid catalysis is concluded to be absent. The data,

Table II. Thermal Interconversion of 2t and 2c at 192.6 ± 0.3 °C in Benzene

t^a	2t	2c	σ^b
0.00	0.004	0.996	
14.4	0.104	0.896	0.001
28.8	0.187	0.813	0.003
43.2	0.237	0.763	0.010
140.4	0.317	0.683	0.006
	0.322[c]	0.678	0.012
0.0	0.998	0.0016	
14.4	0.764	0.236	0.004
28.8	0.612	0.388	0.004
43.2	0.489	0.511	0.001
140.4	0.331	0.669	0.006

$k_{-1} = 1.08 \times 10^{-5}$ s^{-1}
$k_1 = 2.29 \times 10^{-5}$ s^{-1}
$K(c/t) = 2.11$; $r^2 = 0.995$

[a] Time in units of 10^3 s. [b] Deviation from three GLC injections. [c] By integration of three HFT-80 NMR spectra.

collected in Table II, are fit by linear regression to the usual expression for a first-order reversible reaction in which a value of x_e, the concentration of the variable component at equilibrium, is required:

$$\ln [(x_e - x_0)/(x_e - x_t)] = (k_1 + k_{-1})t$$

Because x_e, the fraction at equilibrium, is unknown, it is treated as a second variable. Resulting values of $(k_1 + k_{-1})$ are plotted against r^2, the coefficient of correlation. This procedure is followed starting with both **2t** and **2c**. If the value of $(k_1 + k_{-1})$ common to both experiments is taken, a value of x_e ($[\mathbf{2c}]_e = 0.6784$) is obtained, which lies close to the best values from the **2c** data (0.6797) and the **2t** data (0.6749). Although there is no commonly accepted way of proceeding in a situation such as this, we choose to combine the data from **2c** and **2t** (Table II) for the 4-, 8-, and 12-h points with the equilibrium value, 0.6784, obtained above. The resulting value at 192.6 °C of $(k_1 + k_{-1})$ is 3.37×10^{-5} s^{-1} and of K ($[\mathbf{2c}]_e/[\mathbf{2t}]_e = k_1/k_{-1}$) is 2.11 ($r^2 = 0.9945$). The dissertation of Robertson may be consulted for a more detailed discussion of the handling of the data.[8]

For evaluation of rotational propensity the single rotational epimerizations of (+)-**2c** and (−)-**2t** (to **2t** and **2c**, respectively) are examined. Thanks to good fortune, the singlet chemical shifts of the methyl groups in **2t** and **2c**, which are distinguishable initially (with δ 2.65 and 2.90,

(8) Robertson, L. R., Ph.D. Dissertation, Harvard University, Cambridge, MA, 1981.

Table III. Thermal Rearrangement at 191.8 °C of (+)-2c (Upper Set) and (-)-2t (Lower Set)

	optical purity, %			
t^a	(-)-2t	σ^b	(+)-2c	σ^b
0.00[c]	93.1	1.0	100.0	
25.20	86.6	2.2	98.0	0.5
50.40	84.4	2.7	95.2	0.8
76.03	83.4	1.0	92.2	0.3
131.69	77.4	3.1	82.6	1.7
219.60	70.5	2.4	55.5	1.2
495.43[e]	45.1	1.3	42.4	2.6
0.00[d]	92.1	1.9		
3.42	93.6		82.1	1.1
7.31	92.7		84.1	2.5
29.49	88.9	2.0	81.5	2.6
46.62[f]	86.3	2.1	84.3	1.6
113.20[f]	79.2	1.6	78.3	0.8
251.21[f]	56.5	1.4	63.9	1.0
422.82[f]	42.3	1.7	47.1	2.3

[a] Time in units of 10^3 s. [b] Deviation determined by integration or "cut and weigh" of three spectra. [c] Starting material is (+)-2c containing 3.5% of (-)-2t of 93.1 ± 1% of optical purity. [d] Starting material is (-)-2t. [e] The "76.03" sample recovered and reheated for the total time indicated. [f] The "3.42" sample recovered and reheated for the total lengths of time shown.

respectively, in C_6D_6), become further separated (e.g., δ 2.90 and 4.35, respectively) in response to a chiral lanthanide induced shift (LIS) reagent, europium tris(3-(heptafluorobutyryl)-*d*-camphor) [Eu(hfbc)$_3$][9] and additionally are split into base line separated diastereomeric absorbances. The method is sufficiently sensitive to signal the addition of 2% of racemic **2c** to a sample of (-)-**2c** near to optical purity.

Parenthetically, the roughly fourfold greater sensitivity of **2c** to the same concentration of LIS reagent is fully consistent with a configurational assignment in which the carbomethoxy group of **2t** is the more highly hindered and less favorably disposed to complex with the lanthanide.

The sample of (+)-**2c** employed in the upper set of experiments in Table III is 100 ± 2% of optical purity by chiral LIS and contaminated to the extent of 3.5% (*i*) by (-)-**2t** of 93.1 ± 1% of optical purity (*p*). Only the first four reaction times are considered short enough to warrant being included in the extrapolation to zero time. Each value of the optical purity of (-)-**2t** (x_t) is corrected by estimating the amount (*a*) of **2t** formed by using the previously determined value of ($k_1 + k_{-1}$). Corrected values, x_c, are then obtained from the expression

$$x_c = [a(x_t) - ip]/(a - i)$$

Linear regression of the first four values of x_c gives a corrected value of the optical purity of (-)-**2t** at zero time of 0.878 (*p*), whence $R_A = (1 + p)/1 - p) = 15.4$.

When the starting material is (-)-**2t** of 0.9208 optical purity, each value of the optical purity of (+)-**2c** is corrected simply by dividing by 0.9208. Linear regression of the first five points gives a value of the optical purity of (+)-**2c** at zero time of 0.909 ($R_A = 21.0$); from the first four points, a value of 0.898 lead to $R_A = 18.6$.

These experiments point to a value of $R_A = 18 \pm 3$ and fully substantiate the high value of R_A derivable from the experimental data of Chmurny and Cram.[4] It should be noted that uncertainty in R_A is bound to increase rapidly as R_A increases.

Estimates of the rates of racemization can be made from the data in Table III. (+)-**2c** and (-)-**2t** reveal essentially identical rate constants of 1.88 ($r^2 = 0.931$) and 1.81 ($r^2 = 0.961$) × 10^{-6} s^{-1}, respectively. As rates of enantiomerization, 0.94 and 0.90 × 10^{-6} s^{-1}, respectively, they are so close to those calculated for the slower of the single rotational processes, (+)-**2c** going to (+)-**2t** (0.57 × 10^{-6} s^{-1}) and (-)-**2t** going to (-)-**2c** (1.21 × 10^{-6} s^{-1}) ($k_{-1}/[1 + R_A]$ and $k_1/[1 + R_A]$, respectively), that no quantitatively significant assessment of rates of double rotational processes can be made. A more elaborate effort to extract the relative rates of the double rotational processes may be found in the dissertation.[8] The slower of the two single rotational processes followed by the faster serves as a sufficient model for enantiomerization within the limits of experimental uncertainty. A conservative conclusion is that double rotation in **2c** cannot be greater than 0.2% of single rotation nor greater than 3% in **2t**. In general, experimental difficulties associated with dissecting two consecutive single rotational processes from a double rotational process as the pathway for enantiomerization increases rapidly with higher values of R_A.

Table IV. Thermal Rearrangement of (±)-6c at 258.1 °C and (-)-6c at 255.2 °C

t^a	(±)-6c[c]	(+)-6t[b]	t^a	(-)-6c	(+)-6t
0.00	0.987	0.013	0.00	1.000	
14.40	0.845	0.155	14.82		0.242
33.72	0.710	0.290	34.14		0.202
72.00	0.428	0.572	67.38	0.887	0.170
158.64	0.207	0.793			
360.00	0.097	0.903			

$k_1 = 0.11 \times 10^{-5}$ s^{-1}
$k_{-1} = 1.14 \times 10^{-5}$ s^{-1}
$K(t/c) = 10.8$; $r^2 = 0.968$

[a] Time in units of 10^3 s. [b] Fraction of 6. [c] Fraction of optical purity.

Methyl 2-Phenylcyclopropanecarboxylate. The possibility that the carbomethoxy group alone might have caused the high value of R_A could not be dismissed summarily, because there was no prior experience with the rotational propensity of the ester group either in the cyclopropane or the cyclobutane series. Accordingly, methyl *cis*-2-phenylcyclopropane-1-carboxylate (**6**) has been examined, noting that it is closely related both to the Chmurny-Cram compound and to the well-studied 1-cyano-2-phenylcyclopropane (**7**) (Figure 2).[5,10]

Optically active *trans*-**5** is well-known in the literature.[11] For the convenient preparation of *cis*-**5** and the establishment of its configurational relation to *trans*-**5**, it is useful to pass to and from the stage of the nitriles (**7**) where the trans/cis ratio is 3.

The results of heating (±)- and (-)-*cis*-**6** are given in Table IV. Values for the fraction of *trans*-**6** at equilibrium are determined starting from *trans*-**6** (0.9154) and *cis*-**6** (0.9142) at 255.2 ± 1.0 °C. By the use of an average value of $x_e = 0.915$ (K = [trans/cis] = 10.8) and the usual equation for a reversible first-order reaction, a value of ($k_1 + k_{-1}$) = 1.24 × 10^{-5} s^{-1} ($r^2 = 0.968$) at 258.1 °C is obtained. For the purpose of comparing the rate of this geometrical isomerization with that of the corresponding nitrile, the arbitrary setting of log A = 13.5 leads to a calculated energy of activation, E_a = 45.5 kcal/mol, based on a rate constant half that in value of ($k_1 + k_{-1}$). The similarly derived value for 1-cyano-2-phenylcyclopropane (**7**) is 42.9 kcal/mol [($k_1 + k_{-1}$) = 5.04 × 10^{-6} s^{-1} at 217.8 °C]. The difference may

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(10) Baldwin, J. E.; Carter, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 3942–3944.

(11) Inouye, Y.; Sugita, T.; Walborsky, H. M. *Tetrahedron* **1964**, *29*, 1695–1699.

possibly serve as a suggestion that the carbomethoxy group is less stabilizing of a carbon free radical than is the cyano group by 2.4 ± 1 kcal/mol.

From the behavior of (−)-*cis*-**6** reported in Table IV, the optical purity (p) of (+)-*trans*-**6** formed by preferential internal rotation of the carbomethoxy group is calculated by linear regression of the three data to be 0.256 at zero time. The rotational propensity of the carbomethoxy group vis-à-vis the phenyl group (A = $COOCH_3$, Y = C_6H_5, B = Z = H in Figure 1) may then be calculated: $R_A = 1.69$. Thus, there is nothing out of the ordinary about the rotational propensity of the carbomethoxy group (cf. Table I). If the same sort of internal consistency prevails here as that found by Doering and Barsa[5] in a set of three 1,2-disubstituted cyclopropanes (cyano, phenyl, and isopropenyl), it is predicted that the rotational propensity of cyano should exceed that of the carbomethoxy group by a factor, $R_A = 1.46$.

A value for the rate of racemization of (−)-*cis*-**6** can be calculated from the datum in Table IV ($k = 1.8 \times 10^{-6}$ s^{-1} at 255.2 °C). This value, uncorrected for back-reaction of optically degraded (+)-*trans*-**6**, is a maximum. The double rotational process of (−)-*cis*-**6** has a rate constant $\leq 0.9 \times 10^{-6}$ s^{-1} and is no more than 0.08 times as fast as the predominant single rotational process.

The hydrogen–carbomethoxy carbon bond appears essentially normal in its rotational propensity vis-à-vis hydrogen–phenyl and yet when carbomethoxy and phenyl are coupled on the same carbon the value becomes abnormally large.

1-Cyano-1,2-diphenylcyclopropane. In terms of the model of a continuous diradical serving as transition state,[1,3] both phenyl and carbomethoxy are considered to contribute their radical-stabilizing power to the lowering of the energy of the diradical. Such a stabilized radical should be coplanar and, by extending two dimensionally, might encounter considerable steric difficulty in attempting to rotate past the second radical portion. By contrast, a hydrogen-bearing carbon atom should encounter little resistance to rotating its smaller substituent past the other radical. As a test of such an hypothesis, replacement of the carbomethoxy group by a much narrower group such as cyano seemed appropriate. To that end, the R_A factor of the nitrile corresponding to the Chmurny–Cram ester was sought.

1t and **1c** are converted to the corresponding nitriles, **3t** and **3c** (Figure 2), by conventional means of the ethyl chloroformate, ammonia, and *p*-toluenesulfonyl chloride/pyridine sequence. Happily, incompletely resolved nitriles can be brought to optical purity efficiently by crystallization from benzene/pentane. For purposes of analysis, HPLC is an effective means of separation of **3t** and **3c**, but for the larger amounts needed to measure optical rotation, it is cumbersome. LIS NMR is not sufficiently effective, in part because of the absence of a singlet in the ^{1}H NMR spectra. The obvious device of reconverting the nitriles to the esters, **2t** and **2c**, could not be worked out in satisfactory manner owing to the stubborn resistance of **3t** to quantitative hydrolysis.

The chiral LIS method does work well, however, with the corresponding methyl ketones, **4t** and **4c** (Figure 2). These are conveniently prepared from the nitriles without jeopardy to the chiral centers by reaction with methyllithium. The use of Eu(hfbc)$_3$ permits the establishment of optical purity on the separated diastereomers, **4t** and **4c**, or directly on a mixture of the two.

From data in Table V, by the procedure described for **2**, values of the equilibrium concentration of **3t** that maximize r^2 can be calculated. They agree closely with that value at which $(k_1 + k_{-1})$ is the same whether starting from **3t** or **3c**: $(k_1 + k_{-1}) = 1.05 \pm 0.1 \times 10^{-4}$ s^{-1}; $[\mathbf{3t}]_e = 0.7645$ ($T = 146.0 \pm 0.2$ °C).

Table V. Thermal Rearrangements of 3t and 3c at 145.7 ± 0.5 °C

t^a	3t	3c	σ^b
0.00	0.000	1.000	
2.28	0.185	0.815	0.001
7.56	0.419	0.518	0.013
11.27	0.529	0.471	0.011
0.000	1.000	0.000	
4.57	0.915	0.085	0.006
7.56	0.870	0.130	0.034
11.27	0.847	0.153	0.024
61.20	0.765	0.235	0.008

$k_1 = 2.47 \times 10^{-5}$ s^{-1}
$k_{-1} = 8.03 \times 10^{-5}$ s^{-1}
$K(t/c) = 3.25$, $r^2 = 0.995$

[a] Time in units of 10^3 s. [b] Standard deviation from three HPLC injections.

Table VI. Calculated Values of $\Delta H^{\ddagger}_{av}$ (See Text) of Mono- and Diphenylcyclopropane Esters and Nitriles

cyclopropane 1-	cyclopropane 2-	$(k_1 + k_{-1})^a$	T, °C	K^b	$\Delta H^{\ddagger}_{av}{}^c$	ref
C_6H_5	C_6H_5	3.37	192.6	2.11	38.1	this work
H	$COOCH_3$					
C_6H_5	CN	10.51	146.0	3.25	33.4	this work
H	C_6H_5					
C_6H_5	H	1.24	258.1	10.8	45.0	this work
H	$COOCH_3$					
C_6H_5	H	0.50	217.8	2.79	42.0	10
H	CN					
C_6H_5	H	3.27	192.6	12.7[d]	38.7[e]	12
H	C_6H_5					

[a] In units of 10^{-5} s^{-1}. [b] Equilibrium constant, favored isomer shown. [c] In kcal/mol; calculated for log $A = 13.5$. [d] Calculated from the data of: Crawford, R. L., Lynch, T. R. *Can. J. Chem.* **1968**, *46*, 1457-1458. [e] Rodewald and Depuy give log $A = 11.2$; $E_a = 33.5$ kcal/mol.[12]

For the sake of rough comparison, an average value, $\Delta H^{\ddagger}_{av}$, may be defined: $\Delta H^{\ddagger}_{av} = [(E_a)_1 + (E_a)_{-1}]/2 - RT$. By taking log A = 13.5 for each of the rearrangements, one evaluates an average enthalpy of activation from the formula

$$\Delta H^{\ddagger}_{av} = RT[(\ln 10) \log ([K^{1/2}(k_1 + k_{-1})]/[A(1 + K)]) + 1].$$

The results are shown in Table VI.

In the monophenyl pair, the carbomethoxy group appears to be less stabilizing of a free radical than the cyano group by 3.0 kcal/mol. By contrast, in the diphenyl pair the carbomethoxy group is less effective by 4.7 kcal.

In the cyano pair, the second phenyl group lowers $\Delta H^{\ddagger}_{av}$ by 8.7 kcal/mol, whereas in the carbomethoxy pair, it lowers $\Delta H^{\ddagger}_{av}$ by only 6.9 kcal/mol. In both cases the energy lowering of the second phenyl group is significantly less than the expected value of 13 kcal/mol. When the activation parameters of Rodewald and DePuy[12] are used to calculate $(k_{TC} + k_{CT})$ for 1,2-diphenylcyclopropane at 192.6 °C, the resulting value, 3.27×10^{-5} s^{-1}, is indistinguishable from that of **2**. Given that Arrhenius parameters have not been determined in this work, it is of limited usefulness to speculate on the factors to which the negli-

(12) Rodewald, L. B.; DePuy, C. H. *Tetrahedron Lett.* **1964**, 2951–2953.

Table VII. Thermal Rearrangement of Optically Active 3t and 3c at 145.7 ± 0.5 °C

	optical purity, %			
t^a	3c	σ^b	3t	σ^b
0.00			1.000[c]	
1.06	0.362[d]	0.029		
2.25	0.390[d]	0.022		
7.14	0.405[d]	0.038	0.927[c]	
14.58	0.418[d]	0.031	0.754[c]	0.017
0.00	1.000[e]			
2.25		0.269	0.269[f]	0.047
7.14	0.936[e]		0.352[f]	0.041
14.58	0.830[e]	0.019	0.352[f]	0.010
30.18	0.594[e]	0.021	0.336[f]	0.023

[a] Time in units of 10^3 s. [b] Standard deviation from three NMR spectra. [c] (−)-3t. [d] (+)-3c. [e] (−)-3c. [f] (−)-3t.

gible efficacy of the carbomethoxy group in **2** should be ascribed—whether to the nonadditivity of the stabilizing effect of two substituents on the same carbon atom or to a substantial increase in the barrier to rotation occasioned by the disubstituted carbon atom. The interested reader may welcome referral to recent results of Merényi, DeMesmaeker, and Viehe.[13]

The behavior of samples of optically pure (−)-**3t** and (−)-**3c** when heated at 145.7 °C for varying lengths of time is recorded in Table VII. The configurations of the major product, (+)-**3c** and (−)-**3t**, respectively, correspond to favored single rotation by the hydrogen–phenyl carbon atom bond. The extent of the preference is determined from the optical purity at zero time. It is justifiable to take the average of all eight measurements because the R_A factor is a thermodynamic quantity independent of the epimer serving as starting material. The resulting value, 0.361 ± 0.047, corresponds to R_A = 2.13. Because the starting material is slowly racemizing, there should have been a downward trend with time in the values of optical purity. That effect looks masked by the experimental errors introduced by the somewhat convoluted method of analysis. If the first two, low points are neglected on the grounds of small sample size, the resulting average value, 0.376 ± 0.33, corresponds to R_A = 2.20.

The value of R_A is, in any event, in the low range, far removed from that of the corresponding ester. Neither in this case nor in that of 1,2-dicyano-1-methylcyclopropane (R_A = 1.4)[6] is the presence of a disubstituted carbon atom of itself sufficient to generate a high value of R_A.

Discussion

The explanation for the differences between the ester and the nitrile is unlikely to be found in a change in mechanism from homolytic to heterolytic. Chmurny and Cram find that the rates of rearrangement of the esters, **2t** and **2c**, are insensitive to changes in solvent polarity and conclude that the ester reacts by a homolytic mechanism. Only in the case of considerably greater bias in polarity represented by (*Z*)- and (*E*)-1-cyano-2-phenylcyclopropane-1-carboxylates is strong evidence for a heterolytic mechanism developed.[14]

Chmurny and Cram have already noted that full stabilization by π-electron delocalization requires both the ester and the phenyl group to be coplanar in the plane perpendicular to the axis of the 2p orbitals of the trivalent radical. Fulfillment of this requirement generates a large two-dimensional group, the barrier to rotation of which could be abnormally large. A look at models reveals steric interference to rotation past the second radical regardless whether the phenyl or the ester group is attempting to slip past. By contrast, close approach of the slender, axially symmetrical cyano group encounters no special interference. An equivalent description hypothesizes a partial twisting out of the plane of the ester or the phenyl in order to lessen steric interference, at the cost, however, of a decrease in resonance stabilization. The final effect is a steric retard resulting from the best compromise between reducing interpenetration of van der Waals volumes and losing resonance stabilization. Although models are more convincing, Figure 3 attempts to depict the origin of the hypothetical steric retard.

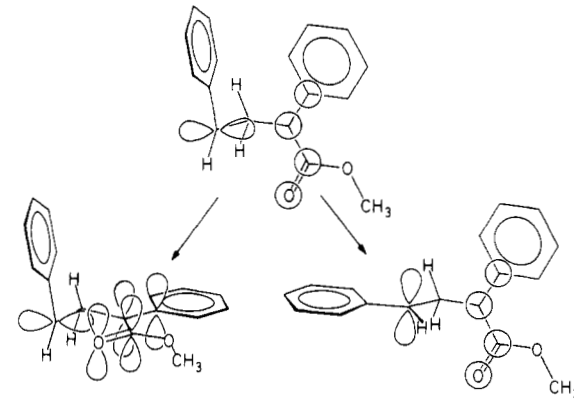

Figure 3. The continuous diradical from **2c** may undergo single internal rotation of the hydrogen–phenyl carbon bond on the right or of carbomethoxy–phenyl carbon bond on the left, the ratios of the two processes (R_A) being 18 ± 3.

In terms of a difference in free energy of activation (or enthalpy of activation, if the difference in entropy of activation is negligible), the sterically more retarded continuous diradical is 2.7 kcal/mol higher in energy. Whether the ester is configured as shown in Figure 3 or the other way round, or whether both contribute their energy-determined share, is not known.

A simple conceptual scheme for these thermal epimerizations is attractive—the major contributor to the activation enthalpy is the need to generate a noninteractive diradical; minor contributors are the various barriers to single and double rotation. Because these minor contributors control the product distribution, rules for the estimation of their relative magnitudes are crucial. To find that steric repulsions play a role encourages the hope that a measure of conceptual control may not be far off.

Experimental Section

Melting points, uncorrected, are determined in a Hershberg apparatus. NMR spectra are obtained in $DCCl_3$ solution on Varian T-60 and HFT-80 spectrophotometers and are reported in ppm from Me_4Si. Preparative GLC is effected on an Aerograph Model A-90-P3 instrument, analytical GLC on a Perkin-Elmer 990 with Hewlett-Packard P-3380S recorder/digital integrator, and HPLC on a Waters ALC-GPC-501 instrument with Model 6000 solvent delivery system and refractive index detector.

(*Z*)- and (*E*)-1,2-Diphenylcyclopropanecarboxylic Acids (1t and 1c). The mixture of methyl esters, **2t** and **2c**, are prepared according to Chmurny and Cram.[4] Partial saponification affords a more convenient method of enrichment than that offered in the literature.[4] At room temperature, saponification of a 1:1 mixture of **1t** and **1c** (100 mg in 0.7 mL ethanol, 1.7 mL water, and 0.12 g NaOH) accompanied by quantitative analysis (NMR: δ CH_3O resonances at 3.2 and 3.5, respectively) after 2 and 4 h affords approximate values of the half-lives: **1t**, 16 h; **1c**, 2 h (for details, pp 70–72, ref 8). The acids are purified by crystallization from

(13) Merényi, R.; DeMesmaeker, A.; Viehe, H. G. *Tetrahedron Lett.* **1983**, *24*, 2765–2768.
(14) Howe, N. E.; Yankee, E. W.; Cram, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 4230–4237.

acetic acid (1 g in 10 mL). At first, flat needles of **1c** appear and can be collected after a few h at room temperature. Upon longer standing cubic crystals of **1t** appear and can be separated manually, if accompanied by needles of **1c**.

1t: mp 153.4–155.2 °C (lit.[4] 150.5–151.5 °C); NMR δ 1.74 (dd, 1), 2.32 (dd, 1), 3.00 (dd, 1), 6.89–7.11 (m, 10).

1c: mp 240–246 °C (lit.[4] 227–228 °C); NMR δ 1.85 (dd, 1), 2.11 (dd, 1), 3.06 (dd, 1), 6.39–7.34 (m, 10).

Resolution of 1t and 1c. The quinine resolution of **1t** follows the procedure of Chmurny and Cram.[4] The resolution of **1c** (3.9 g) is effected partially with *l*-ephedrine (2.89 g) by crystallization from ethanol (175 mL): first crop, 2.5 g, $[\alpha]^{25}_{546}$ +57° (*c* 2.12, $CHCl_3$); after two recrystallizations, 1.1 g, $[\alpha]^{25}_{546}$ + 70° (*c* 1.7, $CHCl_3$). While recrystallization of regenerated acid from acetic acid worsens the optical purity, conversion to the methyl ester **2c** (0.62 g) and two recrystallizations from methanol afford 0.26 g (6.7%) of (+)-**2c**, mp 101.5–102.5 °C (lit.[4] 98.5–99.0 °C), $[\alpha]^{25}_{546}$ +52.3 ± 1.3° (*c* 3.3–4.7, $CHCl_3$) [lit.[4] +55.5° (*c* 0.32, $CHCl_3$)].

Conversion of acid recovered from the ephedrine mother liquor to methyl ester (diazomethane) followed by two recrystallizations from methanol affords 0.6 g of enantiomeric **2c**, mp 101–102 °C (lit.[4] 98.5–99 °C). The rotation of this compound, like that of **1t**, is more than usually sensitive to concentration. From several measurements at concentrations ranging from 11.4 mg/mL to 95.9 mg/mL in $CHCl_3$,[8] a good fit to a parabolic curve is obtained: $[\alpha]^{25}_{546} = -56.65 + 0.094x - 0.000361x^2$, where x is concentration in mg/mL. [The value at $x = 0$ is the "intrinsic rotation" ($c\rightarrow$, $CHCl_3$)].

Chiral Lanthanide Induced Shift (LIS) in 2t and 2c by Europium 3-(Heptafluorobutyryl)-*d*-camphor [Eu(hfbc)$_3$]. Typically, 5–10 mg of methyl ester is dissolved in benzene-d_6 and introduced in an NMR tube by filtering through a plug of glass wool. Eu(hfbc)$_3$ (100 mg), obtained from Norell Chemical Co., Landisville, NJ, is dissolved in benzene-d_6 (0.5 mL) and filtered through a plug of glass wool to provide a stock solution. Although exclusion of air and moisture has little effect on the quality of the spectra, frequent filtration as above and the use of all-glass apparatus are necessary for well-resolved spectra. NMR spectra are measured after each incremental addition of 10–50 μL of stock solution. On racemic samples of **2t** and **2c**, at a molar equivalency of Eu(hfbc)$_3$ of ~0.3, chemical shifts of the CH_3O of 0.33 and 1.7 ppm and enantiomeric splittings of 0.06 and 0.15 ppm, respectively, are obtained. For quantitative estimation of enantiomeric composition, relative areas are determined from enlarged traces by "cut and weigh" or by integration. In all instances at least three spectra are taken of each sample.

Sensitivity of the chiral shift method is estimated by determining an optical purity of 96.7 ± 1% on a 10.537-mg sample from five NMR measurements of chiral LIS, and, then, adding successively 0.059, 0.189, 0.189, and 0.189 mg of racemic **2c** and redetermining the percent of optical purity by NMR (96.4, 96.0, 94.5, 92.9%, respectively). The optical purity of the starting sample can then be calculated to be 98.4% with a standard deviation of ±1.0% and the four successive samples are theoretically, 97.8, 96.1, 94.45, and 92.9% of optical purity, in good agreement with the found values.

(*Z*)- and (*E*)-1-Cyano-1,2-diphenylcyclopropane (3t and 3c). Following the procedure of Doering and Birladeanu,[15] (–)-**1c** (0.5 g), obtained by saponification of optically pure (–)-**2c**, is added to dry methylene chloride (6 mL) and triethylamine (0.73 mL) in a 50-mL round-bottomed flask fitted with side arm, septum, condenser, and magnetic stirrer. Cooled to –25 °C, ethylchloroformate (0.84 mL) is added dropwise by syringe. Stirring is continued for 1 h at –10 to –25 °C.

Anhydrous NH_3 is then passed in for 15 min and stirring is continued for 1 h at room temperature. The mixture is filtered, washed with 6 N HCl, water, and aqueous $NaHCO_3$, dried, and concentrated to give 0.5 g of crude amide: NMR δ 1.73 (dd, 1), 2.10 (dd, 1), 3.10 (dd, 1), 5.33 (br s, 2), 6.51–7.33 (m, 10). A sample of pure racemic amide, mp 149–150 °C, has the same NMR spectrum.

The crude amide (0.5 g) and dry pyridine (0.5 mL) in a 25-mL round-bottom flask with side arm, septum, condenser, and magnetic stirrer are treated at 0 °C with tosyl chloride (0.44 g) in dry pyridine (0.5 mL) over a period of 10 min. After 10 h stirring at room temperature, the mixture is extracted twice with 15-mL portions of ether. The ether extract is washed with 0.1 N HCl, stirred with an equal volume of saturated aqueous $NaHCO_3$ (20 min), washed with water, dried, and concentrated to give crude nitrile, **3c**: mp 113.3 °C after two recrystallizations from benzene/pentane; $[\alpha]^{25}_{546}$ –113.1 ± 0.1° (*c* 1.25–1.78, $CHCl_3$); NMR: δ 2.08 (d, 4), 3.16 (t, 1), 7.24–7.31 (m, 10); IR (KBr) 2250 cm^{-1}.

In a similar sequence, **1t** [1.1 g; $[\alpha]^{25}_{546}$ –266.3° (*c* 5.13, $CHCl_3$)] is converted to the corresponding amide: NMR δ 1.43 (dd, 1), 2.34 (dd, 1), 2.85 (dd, 1), 5.52 (br s, 2), 6.80–7.59 (m, 10); racemic amide similarly prepared, mp 113–115 °C. The amide is then treated in the manner above to give nitrile **3t**, (freed from some unchanged amide by passage through a short silica gel column) which is recrystallized from benzene/pentane: 0.33 mg; mp 86.1 °C; $[\alpha]^{25}_{546}$ –357.8 ± 2.0° (*c* 0.37–1.8, $CHCl_3$); NMR δ (1.97 (dd, 1), 2.16 (dd, 1), 2.77 (dd, 1), 7.26 (s, 10); IR (KBr) 2235 cm^{-1}.

Chiral LIS in (*Z*)- and (*E*)-1-Acetyl-1,2-diphenylcyclopropane (4t and 4c). Although the nitriles **3t** and **3c** are susceptible to LIS reagents, no clean singlet is available for enantiomeric analysis. Attempts to reconvert the nitriles to the esters for analysis succeed with **3c** but cannot be made to proceed past the amide with **3t**. These attempts include acid-catalyzed methanolysis, saponification, treatment with alkaline peroxide, reaction of the amides with nitrous acid, and reaction of **4t** with trimethyloxonium tetrafluoroborate.

4t (25 mg) in 1 mL of anhydrous ether in a dried 10-mL round-bottom flask fitted with a magnetic stirrer and serum cap at 0 °C is treated with 0.2 mL of 1.4 M ethereal methyllithium-/lithium bromide (syringe) followed by stirring for 2 h at 0 °C. The reaction is quenched with 10 drops of concentrated HCl (stirring for 0.5 h at room temperature), diluted with a 3-fold volume of ether, and separated. The ether extract is washed with water (3 times) and saturated aqueous $NaHCO_3$, dried, and concentrated to afford **4t** as a colorless oil (>95%): NMR (benzene-d_6) δ 1.10 (dd, 1), 1.51 (s, 3), 2.46 (dd, 1), 2.73 (dd, 1), 7.10 (s, 10); IR (film) 1700 cm^{-1}.

In similar fashion **3c** affords **1c** as a colorless oil: NMR (benzene-d_6) δ 1.48 (dd, 1), 1.79 (s, 3), 2.05 (dd, 1), 3.25 (dd, 1), 6.42–7.00 (m, 10).

Following the procedures above, the enantiomeric composition of both ketones, either taken separately or as a mixture of the two, can be determined by the chiral LIS technique by using Eu(hfbc)$_3$. As illustration, in the presence of Eu(hfbc)$_3$ (~0.76 molar equiv, ~0.28 M) in benzene-d_6, the induced shifts of **4t** and **4c** and their enantiomeric splits are 0.63 and 0.15 ppm and 1.03 and 0.09 ppm, respectively, (+)-**4t** being upfield of (–)-**4t** and (+)-**4c** being downfield of (–)-**4c**.

A 20-mg sample of **3c**, $[\alpha]^{25}_{546}$ –71.6° (*c* 0.42, $CHCl_3$) 64.3% of optical purity, is converted to **4c** 61.8 ± 2.6% of optical purity by chiral LIS analysis.

Optically Active Methyl *cis*- and *trans*-2-Phenylcyclopropanecarboxylates (6c and 6t). Commercial (Aldrich) 2-phenylcyclopropanecarboxylic acid (**5t**) is resolved by quinine.[5] Replacement of ethanol/hexane by toluene is more convenient: 24 g **5t**, 48 g quinine monohydrate from 650 mL toluene, for example. Successive recrystallizations of the 32-g first crop give 28.8, 16.5, and 15.5 g of salt of optical purity 60.7%, 85.0%, and 90.1%, respectively.

A 4.04-g sample, $[\alpha]^{25}_{546}$ +306.6° (*c* 0.59, EtOH), is converted to amide by a standard procedure[5] (also see above): 2.8 g (70%); mp 132–133 °C.

The amide is dehydrated by P_2O_5 (13.4 g) and triethylamine (45 mL) in dry benzene (90 mL) by heating under reflux for 45 min. After 3 days of stirring at room temperature, the mixture is cooled, quenched carefully with water, and extracted several times with ether. The ether extract is washed with 1.2 N HCl, water, and saturated aqueous $NaHCO_3$, dried, and concentrated to give 2.48 g (95%) of crude nitrile, **7t**. Epimerization to a mixture of **7t** and **7c** is effected by treatment with $NaOCH_3$ in Me_2SO as previously described.[5]

A 0.28-g sample of **7c** in 5 mL of 1:1 concentrated HCl/CH_3OH is boiled under reflux for 34 h. Separation of the methyl ester, **6c**, from unreacted nitrile is effected preparatively on a 4 m ×

(15) Doering, W. von E.; Birladeanu, L. *Tetrahedron* **1973**, *29*, 499–512.

0.25 in. column of 15% Carbowax 20M on Anakrom 50/60 ABS at 200 °C (relative retention time **6c**, 1.0; **7c**, 3.2).

Pure 7c: NMR (benzene-d_6) δ 1.3 (td, 1), 1.5–2.3 (m, 3), 3.1 (s, 3), 6.8–7.2 (m, 5). The optical purity of the sample is determined to be 100% by the chiral LIS method by using $Eu(hfbc)_3$ as described above.

A sample of 6t is obtained in the same manner or by direct methylation (diazomethane) from **7t**: NMR (benzene-d_6) δ 0.85 (td, 1), 1.50 (qd), 1.70 (qd, 1), 2.50 (qd, 1), 3.35 (s, 3), 6.6–7.1 (m, 5). A sample of the (–)-**6t**, 22.6% optically pure by polarimetry, is 22.2 ± 1.6% of optical purity by chiral LIS. In this series the CH_3O resonances of (–)-enantiomers of both **6c** and **6t** are upfield of the (+)-enantiomers.

Thermal Rearrangements. (a) General. Benzene solutions (1.5%) are introduced into Pyrex ampules (previously soaked in 29% aqeuous NH_3, washed thrice with water and thrice with acetone, and dried at 250 °C for several hours), degassed under reduced pressure by three "freeze–thaw" cycles or deoxygenated by infusion of an argon stream for 15 min, and sealed. The sealed ampules, fitted with a hook at one end, are hung in the vapors of a liquid boiling under reflux in a long-necked (46 cm × 5 cm) 1-L round-bottom flask, insulated by asbestos tape and fiberglass batting. The condenser has a hook at the bottom for suspending the ampules by a thin wire. By this arrangement ampules can be introduced and removed conveniently. Temperature is monitored by an iron constantan thermocouple [Leeds and Northrup millivolt potentiometer, Model 8686].

(b) Racemic 2t and 2c. Aliquots (0.5 mL) of a benzene solution (0.85%) of (±)-**2c** (99.6%) are similarly apportioned. The heating liquid is benzonitrile, bp 192.6 °C. Analysis is by a minimum of three injections onto an OV 225 Scott capillary column (50 ft × 0.02 in. ID) at 155 °C. The relative, retention times of **2t** and **2c** are 1.00 and 1.35, respectively. Results are given in Table II. Several runs in ampules made of lead–potash glass (Corning 0120) give identical results. Total recovery is checked in a run with hexamethylbenzene as internal standard. After being heated in a tube furnace at 192 ± 4 °C for 115 h, analysis by NMR (Bruker WH 300) reveals a total recovery of **2t** and **2c** of 99 ± 0.5%.

(c) (–)-2t. Two samples (0.17 and 0.90 g) of (–)-**2t** (92.1% of optical purity by chiral LIS) in 8 and 4 mL of benzene, respectively, in Pyrex ampules (1.9 cm OD, 1.6 cm ID) are heated at 191.8 ± 0.3 °C for 3420 and 7300 s, respectively. An 0.12-g sample of (–)-**3t** recovered from the first tube is dissolved in 13 mL of benzene, apportioned among five ampules (1.1 cm OD, 0.7 cm ID), and heated for additional times between 26 068 and 419 400 s to give the results reported in the second half of Table III.

(d) (+)-2c. A 0.1 g sample of (–)-**2c** (96.5%, 100 ± 2% of optical purity) containing (–)-**2t** (3.5%, 93.1% of optical purity) in 6 mL of benzene is apportioned among six ampules (1.1 cm OD, 0.7 cm ID) and heated at 191.8 °C with the results collected in the upper half of Table III.

(e) 6t and 6c. The position of equilibrium is determined from **6t** and **6c** in a benzene solution with 1-cyanoadamantane as internal standard by heating in vapors of boiling diphenyl ether (258.1 ± 0.5 °C) for 2.6682×10^5 and 3.3882×10^5 s, respectively. From **6t** and **6c**, values of K (=**6t**/**6c**) = 0.9154 and 0.9142 are obtained, respectively.

For determination of the specific rate constant, samples of (±)-**6c** are similarly heated and analyzed on a Perkin-Elmer OV 225 capillary column (150 ft × 0.01 in. ID) at 135 °C (relative retention time **6c**, 1.00; **6t**, 1.33; identical response factors of 0.78 vis-à-vis 1-cyanoadamantane). The results are given in the upper half of Table IV.

Optically pure (by chiral LIS) (–)-**6c** is heated at 255.2 ± 1.0 °C and analyzed by chiral LIS reagent $Eu(hfbc)_3$ as previously described with the results shown in the lower half of Table IV.

(f) Racemic 3t and 3c. In the manner described for **2** (b above), samples of **3** are heated in the vapors of boiling *o*-xylene (146.0 ± 0.2 °C). Too high a temp being required for analysis by GLC, analysis is by HPLC on a Waters' μ-Porasil column (3.9 mm × 30 cm). When eluted with 1:1 hexane/methylene chloride, the retention volumes of **3t** and **3c** are 12.8 and 15.0 mL, respectively, at a flow rate of 3.0 mL/min. A standard mixture prepared with weighed amounts of **3t** and **3c** (50.36 and 49.64%, respectively) has the composition 50.1 and 49.9%, respectively, by HPLC.

A control experiment with 0.3 M hexamethylbenzene as internal standard, heated at 145 ± 3 °C for 138 h, shows a recovery of 106 ± 7%, respectively.

Results are collected in Table V.

(g) (–)-3t. Four samples, 0.1, 0.05, 0.025, and 0.025 g in size, of (–)-**3t** ($[\alpha]^{25}_{546}$ –357.3° (*c* 0.29, $CHCl_3$), 100 ± 2% by chiral LIS) in 3.0, 2.0, 1.0, and 1.0 mL of benzene, respectively, and ampules 1.1 cm OD and 0.7 cm ID in size are heated in vapors of boiling xylene (145.4 ± 0.2 °C) with the results shown in Table VII, first half.

(h) (–)-3c. As in f above, four samples, 0.075, 0.050, 0.025 and 0.025 g, of (–)-**3c** ($[\alpha]^{25}_{546}$ –115.3 ± 1.8 (*c* 1.23, $CHCl_3$), 100 ± 2% by chiral LIS) are heated with results shown in Table VII, second half.

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Registry No. (±)-**1c**, 42333-02-8; (±)-**1t**, 42333-01-7; (±)-**2c**, 42400-68-0; (+)-**2c**, 42333-10-8; (±)-**2t**, 42332-99-0; (–)-**2t**, 42333-04-0; (±)-**3c**, 87421-62-3; (+)-**3c**, 87421-63-4; (–)-**3c**, 87421-64-5; (±)-**3t**, 87421-65-6; (+)-**3t**, 72204-02-5; (–)-**3t**, 87421-66-7; (±)-**4c**, 87395-78-6; (–)-**4c**, 87421-67-8; (±)-**4t**, 87395-79-7; (+)-**4t**, 87421-68-9; (±)-**6c**, 67528-69-2; (–)-**6c**, 67528-62-5; (+)-**6t**, 16205-72-4.