Bond Fixation in Annulenes. 9. Equalization of Ring Inversion and Bond Shifting Energetics in 1,2,3,4-Tetramethylcyclooctatetraene. Asymmetric Synthesis, Direct Resolution, and Absolute Configuration of the Optically Active Hydrocarbon[1]

Leo A. Paquette,* John M. Gardlik,[2a] Larry K. Johnson, and Kevin J. McCullough[2b]

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210. *Received December 10, 1979*

Abstract: Optically active 1,2,3,4-tetramethylcyclooctatetraene (**5***), available by asymmetric synthesis from (-)-*cis*-3,4-dimethylcyclohexene-4,5-dicarboxylic acid (**14***) or preferably by direct resolution with (-)-*endo*-bornyl-1,2,4-triazoline-3,5-dione (**19***), undergoes racemization and bond shifting when heated to 120–160 °C. By appropriate processing of the kinetic data, it is shown that $\Delta G^{\ddagger}_{25}$ for bond shifting (30.9 kcal/mol) and ring inversion (30.9 kcal/mol) have become equal at this level of [8]annulene substitution. This is the first example where an energetic imbalance favoring ring inversion has not prevailed. The absolute configuration of **5*** is also determined and the circular dichroic properties of this dissymmetric (chiral) hydrocarbon are briefly discussed.

While there appears to be a modicum of van der Waals repulsion (2.1 kcal/mol) in the ground state tub conformation (**1**) of cyclooctatetraene (COT), destabilization of this type has been computed to increase markedly (to 11.0 kcal/mol) as the molecule progresses toward planar **2**.[3] The causative factors are expansion

1 **2** **3**

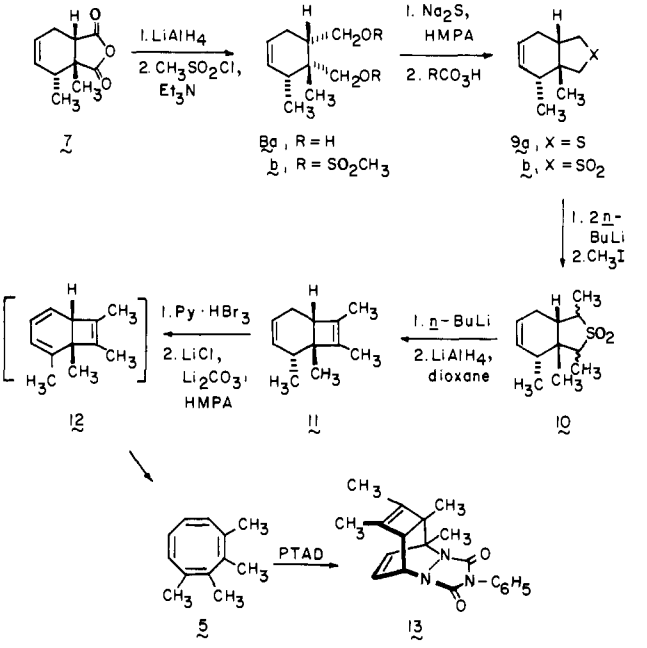
of the internal bond angles from 124 to approximately 135°, enhanced steric compression of the pairs of hydrogens attached to the same double bond, and a buttressing effect of all the hydrogens on their neighbors. The additional bending and stretching constraints demanded by **2** are partly offset by the significant improvement in torsional energy, such that the total energy increase for flattening the COT ring to its planar alternate conformation is less than 13.7 kcal/mol.[4] Monosubstitution of the ring does little to perturb these energetics.[5] In these examples, the $\Delta G^{\ddagger}$ values for conformational ring inversion (RI) which proceeds through transition states having geometry typified by **2** fall in the range of 12.5–14.8 kcal/mol.

The energetics of transforming **1** to planar delocalized form **3** has proven less amenable to computation, with resultant controversy.[3,6] However, bond shifting (BS) within RCOTs, which may involve such transition states, is decidedly more energy demanding ($\Delta G^{\ddagger}$ = 14.9–17.4 kcal/mol).[5] Particular interest is attached to **3** because of its $4n\pi$ electronic nature and possible "negative" resonance energy.

As a consequence of our previous investigation of the dynamic behavior of 1,2,3-Me_3COT,[1,7] it has become clear not only that the magnitudes of the barriers to RI ($\Delta G^{\ddagger}_{25}$ = 24.7 kcal/mol) and BS ($\Delta G^{\ddagger}_{25}$ = 26.5 kcal/mol) are significantly more elevated in this case, but also that the transition states for these processes have become more closely comparable in their energy demands ($\Delta\Delta G^{\ddagger}$ = 1.8 kcal/mol). The presence of methyl groups on three contiguous carbons of the tub-shaped COT framework undoubtedly generates sizably enhanced steric repulsions. As the structure develops planar characteristics, yet more severe van der Waals interactions must result. The contributions of these factors within the hypothetical intermediates 1,2,3-Me_3-**2** and 1,2,3-Me_3-**3** cannot be equivalent. Nevertheless, the activation parameters suggest that the deformations which the molecule must undergo to relieve these rather massive strain increases are becoming more equitable. For this reason, we have viewed with substantial interest the introduction of a fourth contiguously bonded methyl group.

This paper, therefore, describes the preparation of 1,2,3,4-Me_4COT (**5**) in optically active form with known absolute configuration.[8] Determination has been made of the rates of racemization of **5*** and the kinetics of its interconversion with the

Scheme I. Synthesis of Racemic 1,2,3,4-Me_4COT



7 **8a**, R = H; **b**, R = SO_2CH_3 **9a**, X = S; **b**, X = SO_2 **12** **11** **10** **5** **13**

(1) For part 8, see: Paquette, L. A.; Gardlik, J. M. *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) (a) The Ohio State University Dissertation Fellow, 1977–1978. (b) NATO Postdoctoral Fellow of the Science Research Council, 1978–1980.

(3) Allinger, N. L.; Sprague, J. T.; Finder, C. J. *Tetrahedron* **1973**, *29*, 2519.

(4) Anet, F. A. L. *J. Am. Chem. Soc.* **1962**, *84*, 671.

(5) (a) Anet, F. A. L.; Bourn, A. J. R.; Lin, Y. S. *J. Am. Chem. Soc.* **1964**, *86*, 3576. (b) Oth, J. F. M.; Merenyi, R.; Martini, Th.; Schröder, G. *Tetrahedron Lett.* **1966**, 3087. (c) Gwynn, D. E.; Whitesides, G. M.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 2862. (d) Buchanan, G. W. *Tetrahedron Lett.* **1972**, 665. (e) Luz, Z.; Meiboom, S. *J. Chem. Phys.* **1973**, *59*, 1077.

(6) Dewar, M. J. S.; Harget, A.; Haselbach, E. *J. Am. Chem. Soc.* **1969**, *91*, 7521.

(7) Paquette, L. A.; Gardlik, J. M.; Photis, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 7096.

(8) Preliminary reports on the two methods of resolution employed have previously appeared: (a) Gardlik, J. M.; Johnson, L. K.; Paquette, L. A.; Solheim, B. A.; Springer, J. P.; Clardy, J. *J. Am. Chem. Soc.*, **1979**, *101*, 1615. (b) Gardlik, J. M.; Paquette, L. A., *Tetrahedron Lett.* **1979**, 3597.

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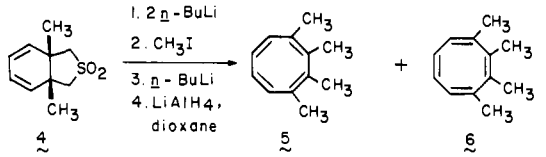
meso-1,2,3,8-Me_4COT isomer. Significantly, equalization of the barriers to BS and RI in **5** has been demonstrated experimentally.[9]

Synthesis of Racemic 1,2,3,4-Me_4COT via Nonsymmetric Intermediates. The original synthesis of 1,2,3,4-Me_4COT relied upon the alkylative desulfonylation of bicyclic diene sulfone **4**.[10]



4 **5** **6**

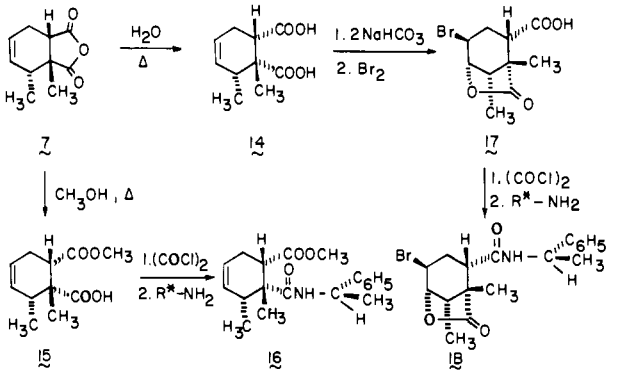
Although a 75:25 mixture of **5** and its bond-shift isomer **6** was obtained in respectable yield and separation of these annulenes could be realized, the symmetrical nature of **4** and its precursors did not allow for introduction of optical activity as needed in the present investigation. To bypass this complication, anhydride **7**, available in good yield by cycloaddition of citraconic anhydride to *trans*-1,3-pentadiene,[11] was selected as starting material. The subsequent sequence of reactions outlined in Scheme I produced the desired hydrocarbon **5** in satisfactory overall yield as the only detectable bond-shift isomer.[12] This welcomed selectivity, which was additionally confirmed by the exclusive production of **13** upon treatment of the unpurified reaction mixture with *N*-phenyltriazolinedione (PTAD), lent strong support to our premise that triene **12** was experiencing ring opening disrotatorily with full 1,3-cyclohexadiene control.

Since 1,2,3,4-Me_4COT did not experience isomerization to **6** upon standing in the absence of air and light at room temperature for prolonged periods, it was evident that π-bond alternation in this [8]annulene is sterically impeded. The difficulty experienced by **5** in attaining a planar conformation is further revealed by its half-wave potential ($E_{1/2}$ = −2.54 V vs. SCE in anhydrous HMPA).[10b] The slightly better reducibility of **6** ($E_{1/2}$ = −2.43 V) may arise from enthalpy differences which have been estimated to favor **6** by 1.0 kcal/mol.[13] Despite the prevailing strain, however, **5** undergoes successful reduction with potassium in ND_3 to its dianion, the ^{1}H NMR spectrum of which is consistent only with a planar or effectively planar geometry on this time scale.[14] Reoxidation of the dianion with iodine in pentane at −55 °C returned a 1:1 mixture of **5** and **6**.[10b]

Preparation of Optically Active 1,2,3,4-Me_4COT and the Assignment of Absolute Configuration. In view of the seemingly enhanced stability of the ground state tub conformation of **5**, the decision was made to incorporate optical activity early in the synthetic sequence, as was accomplished with some success in the preparation of (−)-1,2,3-Me_3COT.[1] This approach was also expected to lend itself conveniently to the assignment of absolute configuration. To this end, **7** was hydrolyzed to diacid **14** by brief heating in water. Three recrystallizations of the diastereomeric mixture of (*R*)-(+)-α-methylbenzylamine salts of **14** from acetone afforded material which was deemed optically pure (further recrystallization changed neither the melting point nor rotation). Acidification returned levorotatory diacid, mp 152–154 °C and $[\alpha]_D$ −110.1°. The dextrorotatory enantiomer of **14***, mp 150–153 °C and $[\alpha]_D$ +110.8°, was obtained with comparable ease by utilization of (*S*)-(−)-α-methylbenzylamide as resolving agent.

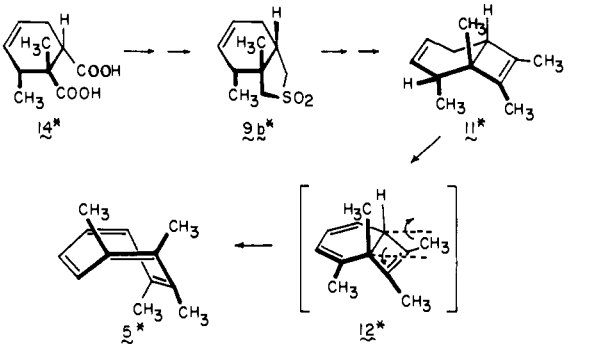
To establish the optical purity of these samples, advantage was taken of the prior observation that **7** could be converted regioselectively (70% yield) to acid ester **15** by heating in methanol (Scheme II). When (−)-**14*** was treated sequentially with acetic anhydride, methanol, oxalyl chloride, and excess (*R*)-(+)-α-

Scheme II. Establishment of the Optical Purity and Absolute Configuration of (−)-14*



7 **14** **17** **15** **16** **18**

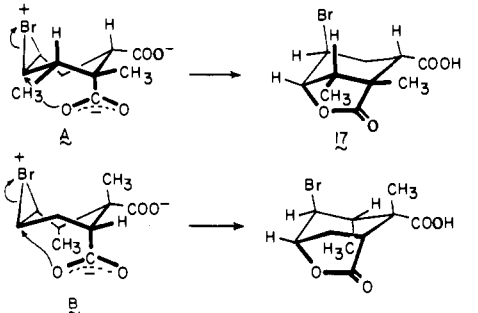
Scheme III. Preparation of Dextrorotatory 1,2,3,4-Me_4COT



14* **9b*** **11*** **5*** **12***

methylbenzylamine, the resulting unpurified **16*** was seen to display a lone methyl ester absorption at δ 3.62 in its ^{1}H NMR spectrum. In contrast, the amide ester obtained by submission of racemic **15** to identical conditions exhibits a pair of methoxyl singlets at δ 3.62 and 3.56 in a 1:1 ratio. Possible complications arising from ring–chain tautomerism of the acid halide of the half-ester[15] were not in evidence. Because the crystals of **16*** proved unsatisfactory for X-ray crystal structure analysis, attention was next turned to an alternative suitable derivative into which an auxiliary chiral center of known absolute configuration could be readily incorporated.

Inspection of molecular models of **14** and knowledge of earlier precedent[16] suggested that bromolactonization of this diacid should proceed with high positional selectivity and give rise predominantly, if not exclusively, to **17**. Neighboring-group participation by the carboxylate anion attached to C_1 must pass through transition state A. The other option involves utilization of the C_6 carboxylate substituent and necessarily entails the activated complex B. Not only does A benefit from less steric crowding, but a product (**17**)



A **17** **B**

is thereby delivered where both methyl substituents and the free

(9) For a preliminary communication on this subject, consult: Gardlik, J. M.; Paquette, L. A.; Gleiter, R. *J. Am. Chem. Soc.*, **1979**, *101*, 1617.

(10) (a) Paquette, L. A.; Photis, J. M.; Ewing, G. D. *J. Am. Chem. Soc.* **1975**, *97*, 3538. (b) Paquette, L. A.; Photis, J. M. *Ibid* **1976**, *98*, 4936.

(11) Huang, W.-Y.; Holmes, H. L.; Fieser, L. F. *J. Am. Chem. Soc.* **1952**, *74*, 5920.

(12) Photis, J. M. Ph.D. Dissertation, The Ohio State University, 1975.

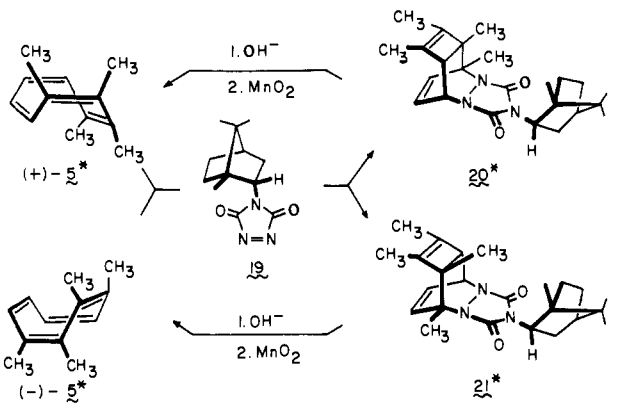
(13) Allinger, N. L., private communication. The entropy difference between this pair of bond-shift isomers is 0.

(14) The ^{1}H NMR spectrum of this dianion recorded in ND_3 solution at −55 °C is illustrated in ref 10a.

(15) See, for example, Chase, B. H.; Hey, D. H. *J. Chem. Soc.* **1952**, 554. Bardhan, J. C. *ibid.* **1928**, 2604. Turner, D. L.; Bhattacharyya, B. K.; Graber, R. P.; Johnson, W. S. *J. Am. Chem. Soc.* **1958**, *72*, 5654. Cason, J. *J. Org. Chem.* **1948**, *13*, 227. Stallberger-Stenhagen, S. *J. Am. Chem. Soc.* **1947**, *69*, 2568.

(16) Corey, E. J.; Sachdev, H. S. *J. Org. Chem.* **1975**, *40*, 579.

Scheme IV. Direct Resolution of 1,2,3,4-Me_4COT

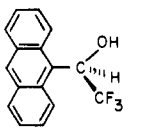


carboxyl are equatorially disposed. At the experimental level, bromolactonization of optically pure (−)-**14*** gave rise to a single product whose sequential treatment with oxalyl chloride and (*R*)-(+)-α-methylbenzylamine furnished **18***. Crystals of this amide proved suitable for three-dimensional crystal structure analysis (courtesy of Professor J. Clardy).[8a] The absolute stereochemistry of **18*** and its precursor molecules (derived from (−)-**14**) is depicted in Scheme II.

The optically active bicyclo[4.2.0]octadiene **11*** obtained via the series of reactions outlined in Scheme III must have the indicated absolute configuration since two chiral centers of the triad present in **14*** are not perturbed until the final ring opening. On the basis of earlier evidence that central bond cleavage in **12*** proceeds under orbital symmetry control (see illustration **12***), the absolute configuration of the resulting 1,2,3,4-Me_4COT, $[\alpha]_D$ +87.8°, must be as indicated.

Direct Resolution of Racemic 1,2,3,4-Tetramethylcyclooctatetraene. The synthesis of **5*** by the sequence outlined in Schemes II and III has the disadvantage that it is inefficient at providing sizable quantities of the optically active [8]annulene. A direct resolution of the racemic hydrocarbon could in principle provide an effective solution to the supply problem. Our application of the optically active triazolinedione procedure[1,8b,17] in this instance was instigated for yet another reason. Although **5** has previously been shown to exist in equilibrium with significant quantities (ca. 25%) of **12** at room temperature,[10] we remained concerned over the relatively low rotatory power shown by (+)-**5***. Unknown to us was the level of ring inversion (with resultant racemization) which could have materialized during the formation of **5*** from **11*** and subsequent isolation. Resolution of this question was clearly of some consequence to our goals.

Treatment of racemic **5** with an equimolar amount of (−)-*endo*-bornyltriazolinedione (**19***) in hexane at 50 °C under nitrogen proceeded smoothly to give the diastereoisomeric adducts **20*** and **21*** as a colorless, viscous oil (Scheme IV). Through successive recrystallizations from ethyl acetate–hexane, hexane, and methanol–water solvent systems, two purified solids were obtained. The first was isolated as lesser soluble long needles, mp 166–168 °C and $[\alpha]_D$ −26.10°, while the second formed fluffy, white crystals, mp 155–157 °C and $[\alpha]_D$ +10.60°. Efforts to determine the diastereomeric purity of these materials by means of lanthanide-induced shifting with tris(3-(trifluoromethylhydroxymethylene)-*d*-camphorato)europium(III) or tris(3-(heptafluoropropylhydroxymethylene)-*d*-camphorato)europium(III) were to no avail. Success was achieved, however, when (*R*)-(−)-1,1,1-trifluoro-2-(9-anthryl)ethanol (**22***)[18] was employed



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(17) Doehner, R.; Jenkins, J., unpublished observations in this laboratory.

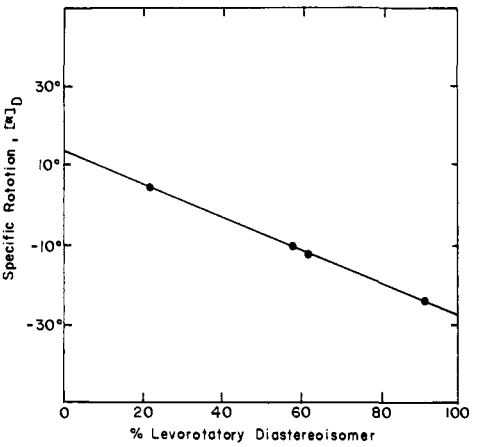


Figure 1. Plot of specific rotation, $[\alpha]_D$, vs. percent of the levorotatory diastereoisomer present in adducts **20*** and **21***.

as a chiral solvating agent in $CDCl_3$. Upon addition of 3 molar equiv of this alcohol to samples of **20***/**21*** of varying diastereomeric purity, the original bridgehead methyl singlet was differentially shifted to give a pair of well-resolved singlets at δ 1.17 and 1.14. Subsequent to planimetric integration of expanded-scale spectra, it proved possible to obtain a linear correlation of diastereoisomeric purity with specific rotation (Figure 1). On this basis, the adduct exhibiting $[\alpha]_D$ −26.10° is seen to be composed of 95% of the levorotatory and 5% of the dextrorotatory diastereoisomers. Likewise, the adduct characterized by $[\alpha]_D$ +10.60° can be estimated to contain a 95:5 mixture of dextro- and levorotatory forms.

When the latter sample was subjected to hydrolysis–oxidation and isolation was achieved by Florisil chromatography at −25 °C (pentane elution) followed by molecular distillation (60 °C at 0.1 Torr), a sample of 1,2,3,4-Me_4COT was obtained which was characterized by $[\alpha]_D$ −310°. Our prior determination of the absolute stereochemistry of (+)-**5*** permits direct assignment of the absolute configuration to the dextrorotatory adduct as **21*** (Scheme III). The levorotatory diastereomer must therefore be **20***. To demonstrate that a sample of (+)-1,2,3,4-Me_4COT could be obtained by this method by resolution, a sample of adduct, $[\alpha]_D$ −12.00°, was subjected to identical hydrolysis–oxidation and workup conditions. The colorless, oily product exhibited $[\alpha]_D$ +54.8°.

Dynamics of Ring Inversion and Bond Shifting in 1,2,3,4-Me_4COT. Quantitative assessment of the dynamic behavior of optically active 1,2,3,4-Me_4COT requires full appreciation of the kinetic intricacies associated with its ring inversion and bond shifting. As illustrated in Scheme V, simple RI through a planar alternate transition state serves to convert (−)-**5** to (+)-**5** at a rate defined as k_1. Under conditions where this COT acquires energy adequate to experience bond shifting, it is presumed that (−)-**5** will undergo conversion not only to (±)-**6**, but to (+)-**5** as well. The rate of this process is defined as k_2. In this instance, consideration must also be given to the isomerization of (±)-**6** to **5**. Because of the obvious structural differences in this pair of molecules, the reverse rate (herein defined as k_{-2}) need not be identical with the forward rate.

In these terms, the rates at which (−)-**5** will decrease its concentration and (+)-**5** will be produced are described by the equations

$$-d[(-)\text{-}5]/dt = 3k_2[(-)\text{-}5] + k_1[(-)\text{-}5] - k_1[(+)\text{-}5] - k_2[(+)\text{-}5] - 2k_{-2}[(\pm)\text{-}6]$$

$$d[(+)\text{-}5]/dt = k_1[(-)\text{-}5] + k_2[(-)\text{-}5] + 2k_{-2}[(\pm)\text{-}6] - k_1[(+)\text{-}5] - 3k_2[(+)\text{-}5]$$

(18) Pirkle, W. H.; Sikkenga, D. L.; Pavlin, M. S. *J. Org. Chem.* **1977**, *42*, 384. We thank Professor Pirkle for providing us with a sample of **22*** which enabled the feasibility studies to be made. Larger quantities of **22*** were purchased from the Aldrich Chemical Co.

Addition provides the following simplification:

$$-\left(\frac{d[(-)\text{-}5] - [(+)\text{-}5]}{dt}\right) = 4k_2[(-)\text{-}5] + 2k_1[(-)\text{-}5] - 4k_2[(+)\text{-}5] - 2k_1[(+)\text{-}5] = 2(2k_2 + k_1)([(-)\text{-}5] - [(+)\text{-}5])$$

Since $\alpha = C[(-)\text{-}5 - (+)\text{-}5]$

$$-\left(\frac{d\alpha}{dt}\right) = -\left(\frac{d[(-)\text{-}5] - [(+)\text{-}5]}{dt}\right) = 2(2k_2 + k_1)\alpha$$

Integration of this expression provides

$$-\ln \alpha = 2(2k_2 + k_1)t - \ln \alpha_0$$

In this instance, the factor 2 is obligatory but for two different reasons. As with the trimethyl derivative, production of the enantiomer not only results in loss of molecule undergoing dynamic change but negates the rotatory power of a second. Isomer **6** is a meso compound and, although its production does result in racemization, additional rotatory power is not lost when it is formed. However, **6** is generated twice as rapidly as enantiomer **5** (see Scheme V and kinetic analysis).

As concerns bond shifting, the rate of appearance of **6** can be shown to be

$$d[\mathbf{6}]/dt = 2(k_2[\mathbf{5}] - k_{-2}[\mathbf{6}])$$

We now allow T to equal the total Me_4COT pool which must be constant:

$$T = [\mathbf{5}] + [\mathbf{6}]; \quad [\mathbf{5}] = T - [\mathbf{6}]$$

On this basis

$$d[\mathbf{6}]/dt = 2(k_2[T - \mathbf{6}] - k_{-2}[\mathbf{6}]) = 2(k_2[T] - (k_2 + k_{-2})[\mathbf{6}])$$

Integration of the above gives

$$[\mathbf{6}] = \frac{k_2[T]}{k_2k_{-2}}(1 - e^{-2(k_2 + k_{-2})t})$$

Kinetic Studies. For determination of the rates of racemization, degassed solutions of (−)-**5*** in purified diglyme were heated at 120, 140, and 160 °C. Plots of $-\ln \alpha$ vs. time gave straight lines whose slopes were equal to $2(k_1 + 2k_2)$. A sample data set is provided in Table III.

For the bond-shifting kinetics, degassed diglyme-d_{14} solutions of **5** were sealed in NMR tubes which were heated in a constant-temperature bath at the same temperatures and individually cooled to −70 °C at appropriate time intervals. The methyl regions of the 60-MHz ^1H NMR spectra of these samples were integrated planimetrically with respect to benzene as the internal standard (Table IV). Such studies, which were made possible by the distinctive chemical shifts of the two isomers, provided for the direct measurement of k_2 and k_{-2}.

The finalized rate data for bond shifting and ring inversion, together with activation parameters, are collected in Tables I and II, respectively. The barriers to these processes in 1,2,3,4-Me_4COT have clearly become equalized ($\Delta\Delta G^{\ddagger}_{25} = 0$) in their free-energy demands. This is a first in [8]annulene chemistry and, as discussed in the ensuing paper,[19] has meaningful implications for the transition-state structures involved.

Chiroptical Properties of (−)-1,2,3,4-Me_4COT. The 1,2,3,4-tetramethyl substitution plan on the cyclooctatetraene tub conformation imparts C_2 symmetry and causes the molecule to be dissymmetric. Since strong ultraviolet absorption in **5** does not appear much before 230 nm (Figure 2), the molecule can be considered to be constructed of four virtually insulated ethylenic subunits. Sight should not be lost of the fact that **5** is in equilibrium with significant amounts of **12** at room temperature. Consequently, both the UV and CD curves (Figure 2) will contain contributions from this valence isomer.

For the unsubstituted tub-shaped COT molecule, the Coulombic coupling of the $\pi \rightarrow \pi^*$ dipoles would give two forbidden and degenerate transitions at long wavelength (**23**) and another two, also degenerate but allowed, at shorter wavelengths (**24**). Chiral

(19) Paquette, L. A.; Gardlik, J. M. *J. Am. Chem. Soc.*, accompanying paper in this issue.

Scheme V. Interconversion Profile of Optically Active 1,2,3,4-Me_4COT

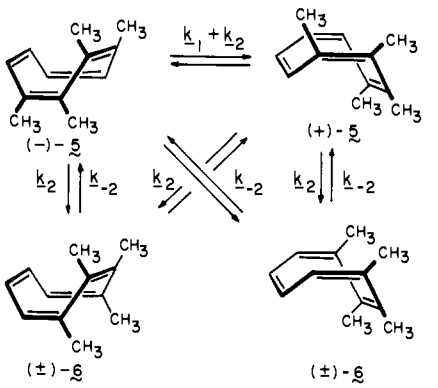


Table I. Rate Date for Bond Shifting in 5 and 6 and Activation Parameters for k_2 in 5

t, °C	fraction of 6 at equilibrium	rate constant for conversion of 5 → 6, k_2, s^{-1}	rate constant for conversion of 6 → 5, k_{-2}, s^{-1}
120	0.56	2.42×10^{-6}	1.99×10^{-6}
		2.56×10^{-6}	2.03×10^{-6}
140	0.64	1.76×10^{-5}	9.9×10^{-6}
160	0.61	7.12×10^{-5}	4.57×10^{-5}

For Bond Shifting in 5
$E_{act} = 28.7$ kcal/mol
$\ln A = 24.4$
$\Delta H^{\ddagger}(25°C) = 28.1$ kcal/mol
$\Delta S^{\ddagger}(25°C) = -13.3$ eu
$\Delta G^{\ddagger}(25°C) = 32.0$ kcal/mol

Table II. Racemization and Ring Inversion Rate Data for 5. Activation Parameters for k_1 in 5

t, °C	measd rate constants for racemization of 5, s^{-1}	rate constants for k_1 in 5, s^{-1}
120	2.43×10^{-6}	4.82×10^{-6}
140	1.76×10^{-5}	2.33×10^{-5}
160	7.12×10^{-5}	1.51×10^{-4}

For Ring Inversion in 5
$E_{act} = 29.1$ kcal/mol
$\ln A_1 = 29.4$
$\Delta H^{\ddagger}(25°C) = 28.5$ kcal/mol
$\Delta S^{\ddagger}(25°C) = 11.0$ eu
$\Delta G^{\ddagger}(25°C) = 31.8$ kcal/mol

Table III. Exemplary Rate Data for Racemization of (−)-5* (120.4 ± 0.2 °C)

time, s	α_{436}, deg	$\ln \alpha_{436}$
0	−0.120	−2.120
7 200	−0.107	−2.235
14 400	−0.091	−2.397
21 600	−0.078	−2.551
28 800	−0.070	−2.659
36 000	−0.059	−2.830
43 200	−0.051	−2.976
50 400	−0.046	−3.079
57 600	−0.040	−3.079
144 000	0.000	−3.219

slope = 1.936 (±0.027) × 10^{-5} s^{-1}
y intercept = −2.116 (±0.009)
r = 0.999 104

Table IV. Exemplary Rate Date for Interconversion of 5 and 6 (120.0 ± 1.0 °C)

$$X = [6] = \frac{\text{area of methyl singlet at } \delta\ 1.80}{\text{area of internal standard } (C_6H_6)}$$

time, s	area of internal standard	area of singlet at δ 1.80	ln $[X_{eq}/(X_{eq} - X)]$
0	68	0	0.0000
7 200	73	17	0.1096
14 400	68	25	0.1790
29 600	72	46	0.3183
43 200	78	63	0.4461
50 400	74	69	0.5364
57 600	78	78	0.5896
64 800	76	81	0.6449
72 000	83	91	0.6707
86 400	82	103	0.8198
108 000	78	112	1.0219
284 400 (eq)	73	164	

slope = 9.18 (±0.21) × 10^{-6} s^{-1} fraction of 6 at equilibrium = 0.56
y intercept = 0.04 (±0.01)
r = 0.997 608

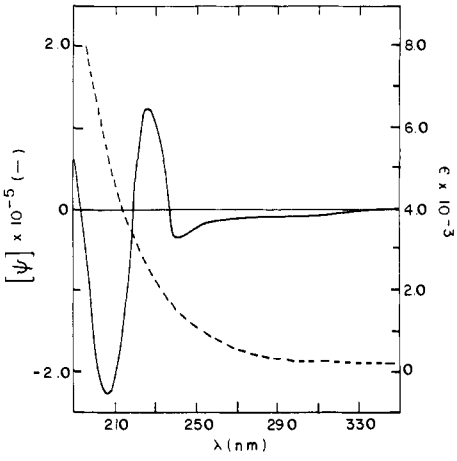
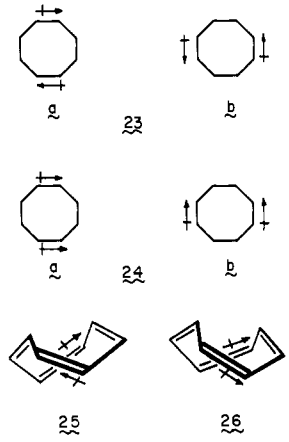


Figure 2. The UV (--) and CD spectra (—) of (-)-1,2,3,4-tetramethylcyclooctatetraene (**5***) recorded in *n*-hexane.

ring torsions due to substitution, if unequal in the several bonds, would split both degeneracies and give opposite rotational strengths to **23a** and **23b**, and also to **23a/24a** and **23b/24b** as denoted by **25** and **26**. Although the CD spectrum of (-)-**5*** shows the



expected pattern (signs are evident of a fourth band in the vacuum-UV region), the complication introduced by the presence of **12** and our ignorance of the relative torsions around the ring generated by the substituents' spatial requirements, etc., make the observed CD bands difficult to rationalize at the present time.

Experimental Section

Melting points and boiling points are uncorrected. Proton magnetic resonance spectra were obtained with Varian T-60, Varian EM-360, and Bruker HX-90 spectrometers; apparent splittings are given in all cases. Infrared spectra were determined on a Perkin-Elmer Model 467 instrument. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Optical rotations were measured on Perkin-Elmer Model 141 and 241 polarimeters. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***cis*-3,4-Dimethyl-4,5-bis(methanesulfonyloxymethyl)cyclohexene (8b).** To a mechanically stirred refluxing slurry of 38.0 g (1.0 mol) of lithium aluminum hydride in 2 L of tetrahydrofuran was added dropwise under nitrogen a solution of 140 g (0.778 mol) of anhydride **7**[11] in 500 mL of tetrahydrofuran. The reaction mixture was refluxed for 20 h and cooled; the excess hydride was decomposed by the careful addition of saturated sodium sulfate solution, followed by stirring until the salts were white. The salts were removed by vacuum filtration, the filtrate was dried, and the solvent was removed in vacuo to yield 107.3 g (81%) of diol **8a** as a nearly colorless oil.

To a solution of this diol in 2.5 L of dichloromethane cooled to -10 °C (ice–salt bath) was added 229 g (2.08 mol) of triethylamine under nitrogen and the reaction mixture was stirred for 10 min. Methanesulfonyl chloride (175 g, 1.53 mol) was added dropwise over a period of 0.5 h and stirring was maintained at -10 °C for 1 h. The cold reaction mixture was poured onto ice water (2.5 L) and the layers were separated. The aqueous layer was extracted with dichloromethane (2 × 500 mL). The combined organic phases were washed with ice-cold 10% hydrochloric acid solution (1 L), 5% sodium bicarbonate solution (1 L), and ice water (1 L) before drying. The solvent was removed in vacuo to yield 160.7 g (78%) of dimesylate **8b** as a viscous, yellow oil: ^{1}H NMR (δ, $CDCl_3$) 5.85–5.20 (m, 2 H), 4.65–3.86 (m, 4 H), 3.01 (s, 6 H), 2.50–1.85 (br m, 4 H), 1.19 (s, 3 H), and 0.98 (d, J = 7.0 Hz, 3 H). This material was used for the next step without further purification.

Comparable reduction of **14*** (14.27 g, 0.072 mol), $[\alpha]_D$ -110.0°, yielded 12.11 g (99%) of diol **8a*** as a nearly colorless oil, $[\alpha]_D$ -51.5° (*c* 79.4, C_2H_5OH).

The optically active diol was treated with 20.7 g (0.205 mol) of triethylamine and 17.2 g (0.150 mol) of methanesulfonyl chloride in 350 mL of dichloromethane as described above. There was obtained 21.5 g (93%) of **8b*** as a viscous, yellow oil, $[\alpha]_D$ -29.4° (*c* 89.0, C_2H_5OH).

***cis*-1,2-Dimethyl-8-thiabicyclo[4.3.0]non-3-ene 8,8-Dioxide (9b).** An anhydrous slurry of sodium sulfide in hexamethylphosphoramide (HMPA) was prepared by distillation of the water-HMPA fraction (bp 36–132 °C, 30 mm) from a mixture of 360 g (1.5 mol) of $Na_2S{\cdot}9H_2O$ and 2 L of HMPA. Oily dimesylate **8b** (160.7 g, 0.493 mol) was added to the cooled slurry in one portion. After being heated with stirring at 120 °C for 24 h under nitrogen, the reaction mixture was cooled, poured onto 2.5 L of ice water, and extracted with pentane (3 × 1 L). The combined extracts were washed with water (5 × 2 L) and saturated salt solution (1 × 1 L) before drying. The solvent was removed in vacuo and the residue was distilled to yield 58.9 g (71%) of **9a** as a colorless liquid, bp 80–95 °C (1.0 mm).

To a mechanically stirred solution of 58.9 g (0.353 mol) of **9a** in 400 mL of ether cooled to 0 °C was added 1.14 L of a 0.62 M solution of monoperphthalic acid in ether (0.706 mol). After the addition was complete, the reaction mixture was stirred at room temperature for 6 h and allowed to stand for 12 h. The precipitated phthalic acid was removed by vacuum filtration and the filtrate was concentrated in vacuo to a thick paste. Dichloromethane (1 L) was added to the paste and the resulting solution was washed with 0.5 M sodium hydroxide solution (2 × 1 L) and water (1 × 1 L) prior to drying. The solvent was removed in vacuo to yield 67.8 g (96%) of **9b** as a white solid. The analytical sample was obtained by recrystallization from ether as a highly crystalline solid: mp 142–145 °C; ^{1}H NMR (δ, $CDCl_3$) 5.85–5.13 (m, 2 H), 3.70–2.55 (m, 4 H), 2.52–2.00 (m, 4 H), 1.40 (s, 3 H), and 0.98 (d, J = 7.2 Hz, 3 H).

Anal. Calcd for $C_{10}H_{16}O_2S$: C, 59.97; H, 8.05; S, 16.01. Found: C, 59.93; H, 7.99; S, 15.87.

Reaction of the unpurified optically active dimesylate **8b*** (21.0 g, 0.0644 mol) under comparable conditions furnished 11.04 g (86.6%) of **9b*** as a colorless, crystalline solid, mp 89–91 °C (from ether), $[\alpha]_D$ -11.2° (*c* 65.0, CH_2Cl_2).

1,2,7,8-Tetramethylbicyclo[4.2.0]octa-3,7-diene (11). To a magnetically stirred solution of 67.8 g (0.339 mol) of **9b** in 800 mL of dry tetrahydrofuran was added 424 mL of a 1.6 M solution of *n*-butyllithium in hexane (0.678 mol) via cannula at -78 °C under nitrogen. The solution was stirred at -78 °C for 0.5 h and 100 mL (excess) of methyl

iodide in 100 mL of dry tetrahydrofuran was added dropwise over a period of about 0.5 h. After the addition was complete, the reaction mixture was stirred at −78 °C for 1 h, allowed to come to room temperature, and stirred for an additional 4 h. Water (50 mL) was added and most of the tetrahydrofuran was removed in vacuo. The residue was dissolved in dichloromethane (1 L); the organic phase was washed with water (2 × 1 L) and dried. The solvent was removed in vacuo to yield 71.0 g (92%) of **10** as a viscous, yellow oil.

A solution of **10** in 300 mL of dry dioxane was treated with 194 mL of a 1.6 M solution of *n*-butyllithium in hexane (0.311 mol) via cannula with external cooling (ice bath) under nitrogen. The orange solution was allowed to come to room temperature, transferred via cannula to a pressure-equalized addition funnel, added dropwise over a period of 20 min to a refluxing slurry of 59.3 g (1.56 mol) of lithium aluminum hydride in 3 L of dry dioxane under an atmosphere of nitrogen, and refluxed for 20 h. The reaction mixture was cooled and excess hydride was destroyed by the careful addition of Glauber's salt followed by stirring until the salts were white. The precipitate was removed by vacuum filtration and washed with pentane (2 × 300 mL). The filtrate was divided in half and each half was poured onto water (2 L) and extracted with pentane (3 × 600 mL). The combined organic layers were washed with water (5 × 2 L) and saturated salt solution (2 L) before drying. The solvent was removed in vacuo and the residue was chromatographed on 770 g of alumina (neutral, activity I). Elution with pentane and distillation of the eluate yielded 11.4 g (23%) of **11** as a colorless liquid: bp 35–60 °C (0.7 mm); ^{1}H NMR (δ, CCl_4) 5.75–5.20 (m, 2 H), 2.35–1.20 (m, 4 H), 1.67–1.30 (m, 6 H), 1.15 (s, 3 H), and 0.90–1.08 (m, 3 H).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.10. Found: C, 88.84; H, 11.21.

Submission of 10.5 g (0.0525 mol) of optically active **9b***, $[\alpha]_D$ −11.2°, to the predescribed conditions and preparative VPC isolation (11 ft × 0.25 in., 5% XF 1150 on Chromosorb G, 50 °C) afforded 81 mg (6%) of 11*, $[\alpha]_D$ −109.3° (*c* 38.2, pentane).

1,2,3,4-Tetramethylcyclooctatetraene (5). To a magnetically stirred solution of 11.4 g (0.0705 mol) of **11** in 400 mL of carbon tetrachloride and 400 mL of glacial acetic acid was added 22.6 g (0.0705 mol) of pyridinium hydrobromide perbromide in one portion and stirring was maintained at room temperature until all the solid had dissolved (about 2 h). The reaction mixture was poured onto water (700 mL), the layers were separated, and the aqueous layer was extracted with carbon tetrachloride (2 × 350 mL). The combined organic layers were washed with water (500 mL), 5% sodium bicarbonate solution (500 mL), and water (500 mL) prior to drying. The solvent was removed in vacuo to yield 22.4 g (99%) of dibromide as a yellow oil.

This dibromide was added in one portion to a mechanically stirred slurry of 18.2 g (0.7 mol) of lithium fluoride, 51.8 g (0.7 mol) of lithium carbonate, and 0.5 g of powdered glass in 1 L of HMPA (distilled from CaH_2). The reaction mixture was stirred and heated at 50–55 °C under nitrogen for 20 h, cooled, poured onto ice–water (1 L), and extracted with pentane (3 × 1 L). The combined organic layers were washed with water (10 × 1 L) and saturated salt solution (1 L) prior to drying. The solvent was removed in vacuo to yield a yellow oil which was chromatographed on 300 g of Florisil. Elution with pentane (fraction size 250 mL) afforded in fractions 2–5 a nearly colorless liquid which was distilled to give 7.69 g (69%) of **5**: bp 35–40 °C (1.0 mm); ^{1}H NMR (δ, CCl_4) 6.00–5.40 (m, 4 H), 1.67 (m, 6 H), and 1.58 (s, 6 H), also 5.60–5.25 (weak m), 2.70 (weak br s), and 1.20 (s) due to a small amount of the bicyclic valence isomer present.[10]

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.46; H, 10.08.

The optically active hydrocarbon obtained with the highest rotation by this method was prepared as follows. To a solution of 64 mg (0.39 mmol) of **11***, $[\alpha]_D$ −109.3° (*c* 38.2, pentane), in 3 mL of carbon tetrachloride and 3 mL of glacial acetic acid was added 145 mg (0.454 mmol) of pyridinium hydrobromide perbromide and the resulting mixture was stirred at room temperature for 1.5 h. After dilution with five volumes of water, the organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 30 mL). The combined organic layers were washed with 5% sodium bicarbonate solution, water, and saturated salt solution before drying. The solvent was removed in vacuo to yield a yellow oil which was heated with 0.16 g (3.9 mmol) of lithium chloride, 0.29 g (3.9 mmol) of lithium carbonate, 115 mg of powdered glass, and 4 mL of HMPA at 60 °C for 15 h under nitrogen. After the solution was cooled to room temperature, water (50 mL) was added and the solution was filtered to remove the glass. The aqueous solution was extracted with pentane (4 × 20 mL). The combined organic layers were washed with water (10 × 50 mL) and saturated salt solution (50 mL) prior to drying. The solvent was removed in vacuo and the residue was distilled (40 °C, 0.3 mm) to yield 52 mg (83%) of **5***, $[\alpha]_D$ +87.8° (*c* 7.8, pentane). The UV and CD spectra were obtained using this sample.

Table V

$[\alpha]_D$, deg	% 21* present	% 20* present
+4.30	78	22
−10.40	41.6	58.4
−12.85	38	62
−24.43	8.6	91.4

***N*-Phenyltriazolinedione Adduct of 1,2,3,4-Tetramethylcyclooctatetraene.** To a magnetically stirred solution of 2.56 g (0.016 mol) of **5** in 50 mL of hexane heated at 50 °C under nitrogen was added a solution of 3.02 g (0.0173 mol) of freshly sublimed *N*-phenyltriazolinedione in 50 mL of ethyl acetate over a period of about 1 h. After the addition was complete, the solution was stirred and heated at reflux for 4 h, cooled, and deposited on 20 g of Florisil by evaporation. This mass was placed atop a column of 200 g of Florisil. Elution with hexane (700 mL) yielded only hydrocarbon impurities. Elution with 50% ethyl acetate in hexane (1000 mL) afforded 4.0 g of crude product as a yellow solid. This material was recrystallized from ethyl acetate–hexane to give 1.83 g (34%) of white crystals: mp 189–191 °C; ^{1}H NMR (δ, $CDCl_3$) 7.57–7.20 (m, 5 H), 6.08 (d, J = 3.5 Hz, 2 H), 4.98 (q, J = 3.5 Hz, 1 H), 2.60 (br d, J = 4.0 Hz, 1 H), 1.80 and 1.33 (s, 3 H each), and 1.49 (s, 6 H).

Anal. Calcd for $C_{21}H_{21}N_3O_2$: C, 72.60; H, 6.09; N, 12.10. Found: C, 72.71; H, 6.07; N, 12.18.

Hydrolysis–Oxidation of 13. A slurry of 200 mg (0.6 mmol) of **13** and 200 mg of sodium hydroxide in 16 mL of isopropyl alcohol was refluxed under nitrogen for 1 h. The solution was cooled, made acidic (pH 1) by careful addition of 3 N hydrochloric acid, and then made basic (pH 9) by the careful addition of 3 N ammonium hydroxide. Pentane (20 mL) and 500 mg of manganese dioxide were added, and the reaction mixture was stirred at room temperature for 1 h under an atmosphere of nitrogen. The slurry was poured onto cold water (10 mL), the layers were separated, and the aqueous layer was extracted with pentane (2 × 20 mL). The combined organic phases were washed with water (3 × 60 mL) and saturated salt solution (60 mL) before drying. The solvent was removed in vacuo and the residue was chromatographed on 3 g of Florisil. Elution with pentane afforded 80 mg (83%) of **5** which was identical in all respects with the original sample and was very clean.

***cis*-3,4-Dimethylcyclohexene-4,5-dicarboxylic Acid (14).** A suspension of 132 g (0.733 mol) of **7** in 1 L of water was heated at reflux for 2 h. The clear solution was allowed to cool slowly to room temperature, which caused the diacid to crystallize as a fine, white powder. Recrystallization of this material from hot water furnished 102 g (70%) of colorless solid, mp 185–188 °C dec (lit.[11] mp 187–188 °C dec).

2-Carbomethoxy-1,6-dimethyl-4-cyclohexene-1-carboxylic Acid (15). A solution of 9.0 g (0.05 mol) of **7** in 90 mL of absolute methanol was refluxed for 24 h. The methanol was removed in vacuo and the remaining oil was crystallized from hexane. The resulting solid was recrystallized from ether–hexane to yield pure **15**: mp 101–102 °C; ^{1}H NMR (δ, $CDCl_3$) 11.79 (s, 1 H), 5.88–5.18 (m, 2 H), 3.64 (s, 3 H), 2.9–2.0 (m, 4 H), 1.27 (s, 3 H), and 1.04 (d, J = 7 Hz, 3 H).

Resolution of 14. To a warm solution of 99.0 g (0.5 mol) of **14** in 1200 mL of acetone was added a solution of 60.5 g (0.5 mol) of (*R*)-(+)-α-methylbenzylamine in 500 mL of acetone and the resulting solution was heated to boiling on a steam bath for a few minutes. The solution was allowed to cool slowly to room temperature, which caused 77 g of fluffy, white solid to deposit. This material was twice recrystallized from acetone to give 25.1 g (18%) of pure salt, mp 169–170 °C, $[\alpha]_D$ −5.53° (*c* 18.5, CH_3OH).

Enantiomerically pure **14*** was obtained by treating an aqueous solution of the salt with 10% hydrochloric acid and extraction with ether. Recrystallization from hot water yielded (−)-**14***, mp 152–154 °C, $[\alpha]_D$ −110.1° (*c* 98.2, C_2H_5OH).

The (+) enantiomer of **14*** was obtained by a similar resolution, using (*S*)-(−)-α-methylbenzylamine. Recrystallization from hot water afforded (+)-**14***, mp 150–153 °C, $[\alpha]_D$ +110.8° (*c* 25.8, C_2H_5OH).

Determination of Optical Purity of (−)-14*. A solution of 1.04 g (0.0049 mol) of resolved diacid **14***, $[\alpha]_D$ −110.0°, in 40 mL of acetic anhydride was heated at reflux for 2 h. The solvent was removed under high vacuum. The crude anhydride was then refluxed for 24 h with 20 mL of absolute methanol. The methanol was removed in vacuo to give **15***, which was stirred at room temperature with 3.17 g (0.25 mol) of oxalyl chloride in 10 mL of dry benzene for 1 h. The solvent and excess oxalyl chloride were removed in vacuo. The acid chloride was dissolved in 10 mL of dry benzene and treated with 0.6 g (0.005 mol) of (*R*)-(+)-α-methylbenzylamine and 1 mL of pyridine with stirring at room temperature for 1 h. Ether was added and the solution was washed twice with 5% hydrochloric acid solution, 5% sodium bicarbonate solution,

water, and saturated salt solution before drying. The solvent was removed in vacuo to yield 1.4 g (91%) of **16** as a yellow oil whose ^1H NMR spectrum (in $CDCl_3$) exhibited only one methyl ester resonance at δ 3.62. When this amide was prepared from racemic half-acid ester **15** under similar conditions, a material was obtained whose ^1H NMR spectrum exhibited two methyl ester resonances at δ 3.62 and 3.56 but was otherwise superimposable.

Bromolactone Amide 18. To a well-stirred solution of 0.4 g (2 mmol) of (−)-**14*** $[\alpha]_D$ −110.0°, in 2 mL of water containing 0.42 g (5 mmol) of sodium bicarbonate was added dropwise 0.336 g (2.1 mmol) of bromine. After the addition was complete, the solution was stirred for 45 min and made acidic (pH 4–5) by the careful addition of 5% hydrochloric acid, which caused a yellow solid to precipitate. This solid was collected by vacuum filtration and dissolved in dichloromethane. The organic solution was washed with water and dried. Solvent was removed in vacuo to yield 0.51 g (92%) of bromolactone **17*** as a white powder. Recrystallization of this material from ethyl acetate furnished a white solid, mp 233–235 °C, $[\alpha]_D$ −25.68° (*c* 25.9, CH_2Cl_2).

To a solution of 0.13 g (0.47 mmol) of **17*** in 10 mL of dry dichloromethane was added 0.30 g (2.34 mmol) of oxalyl chloride. This solution was stirred at room temperature for 16 h, and the solvent and excess oxalyl chloride were removed in vacuo. The acid chloride was dissolved in 10 mL of dry benzene and treated with 0.17 g (1.41 mmol) of (*R*)-(+)-α-methylbenzylamine and 1 mL of pyridine. The reaction mixture was stirred at room temperature for 3 h and poured onto ice-cold 5% hydrochloric acid (50 mL). The aqueous solution was extracted with dichloromethane (2 × 50 mL). The combined organic phases were washed with 5% hydrochloric acid (50 mL), 5% sodium bicarbonate solution (50 mL), and saturated salt solution before drying. The solvent was removed in vacuo to yield 0.16 g (89.4%) of colorless solid which was recrystallized from ethyl acetate–hexane to give pure **18***: mp 182.5–183 °C; $[\alpha]_D$ +10.75° (*c* 14.6, CH_2Cl_2); ^1H NMR (δ, $CDCl_3$) 7.18 (br s, 5 H), 5.14–4.75 (m, 1 H), 4.52–4.17 (m, 2 H), 3.02–1.96 (m, 5 H), 1.42 (d, *J* = 7.0 Hz, 3 H), 1.16 (s, 3 H), and 1.05 (d, *J* = 7.0 Hz, 3 H).

Anal. Calcd for $C_{18}H_{22}BrNO_3$: C, 56.85; H, 5.83; N, 3.68. Found: C, 56.77; H, 5.85; N, 3.68.

Direct Resolution of 1,2,3,4-Tetramethylcyclooctatetraene. A solution of 5.13 g (0.0320 mol) of **5** in 150 mL of hexane was heated at 50 °C under nitrogen and a solution of 8.20 g (0.035 mol) of freshly sublimed (−)-*endo*-bornyltriazolinedione (**19***) in 150 mL of ethyl acetate was added dropwise over a period of 1 h with stirring. After the addition was complete, the reaction mixture was refluxed under nitrogen for 20 h, allowed to cool, and concentrated in vacuo to yield a viscous, orange oil. The product was deposited on 40 g of Florisil, and this mass was placed atop a column of 400 g of Florisil. Elution with hexane (1000 mL) yielded only hydrocarbon impurities. Elution with 10% ethyl acetate in hexane (2000 mL) yielded 6.0 g of a nearly colorless oil, whose ^1H NMR spectrum indicated it to be the **20***/**21*** mixture. This colorless oil was dissolved in warm hexane, concentrated to a very small volume on a steam bath, and allowed to cool slowly. White solid (750 mg), mp 148–158 °C, $[\alpha]_D$ −21.57° (*c* 8.9, C_2H_5OH), was deposited.

Four recrystallizations of this material from ethyl acetate–hexane gave 200 mg (1.6%) of long, crystalline needles: mp 166–168.5 °C; $[\alpha]_D$ −26.10° (*c* 7.2, C_2H_5OH); ν_{max} (KBr) 3000–2900, 1775, 1715, 1435, and 1400 cm^{-1}; ^1H NMR (δ, $CDCl_3$) 6.00 (d, *J* = 4.0 Hz, 2 H), 4.85 (q, *J* = 4.0 Hz, 1 H), 4.26–4.09 (m, 1 H), 2.60–2.40 (m, 1 H), 2.04–1.56 (m, 7 H), 1.75 (s, 3 H), 1.48 (s, 6 H), 1.28 (s, 3 H), 0.95, 0.87, and 0.79 (s's, 3 H each); calcd *m/e* 395.257 36, obsd 395.257 85.

Anal. Calcd for $C_{24}H_{33}N_3O_2$: C, 72.87; H, 8.41; N, 10.62. Found: C, 72.85; H, 8.39; N, 10.56.

This sample was estimated to contain 95% of diastereoisomer **21*** and 5% of diastereoisomer **20***, using the correlation curve provided in Figure 1.

Additional hexane was added to the original mother liquor and the solution was placed in a freezer to crystallize. White crystals (500 mg) which deposited in the cold were isolated by vacuum filtration, mp 130–144 °C, $[\alpha]_D$ +4.30° (*c* 11.4, C_2H_5OH).

This sample was recrystallized four times from methanol–water to give 145 mg (1%) of fluffy, white crystals, mp 155–157 °C, $[\alpha]_D$ +10.60° (*c* 8.3, C_2H_5OH), whose IR, NMR, and mass spectra were identical with those of the above sample.

This material was estimated to contain 5% of diastereoisomer **21*** and 95% of diastereoisomer **20***.

Determination of Diastereoisomeric Purity of 20* and 21*. A series of NMR tubes containing adduct samples of different rotations and (*R*)-(−)-1,1,1-trifluoro-2-(9-anthryl)ethanol (**22***) was prepared in the following way. A solution of 20 mg (0.05 mmol) of the adduct and 45 mg (0.15 mmol, 3 molar equiv) of **22*** in 0.3 mL of chloroform-*d* containing 1% Me_4Si was filtered into an NMR tube and a 90-MHz ^1H NMR spectrum was obtained. The effect of the optically active alcohol was to cause the peaks assigned to the bridgehead methyl group to separate into two peaks at δ 1.17 and 1.14, corresponding to each of the diastereoisomeric adducts. This region was expanded, the two peaks were integrated, using a planimeter, and the percent of diastereoisomer **20*** was plotted vs. specific rotation, $[\alpha]_D$. The points in Table V were obtained.

When the specific rotation was plotted as a function of the percent of diastereoisomer **20*** present, a linear correlation within the estimated accuracy of the experiment was obtained (Figure 1).

Hydrolysis–Oxidation of (−)-*endo*-Bornyltriazolinedione Adducts 20* and 21*. A slurry of 100 mg (0.25 mmol) of the adduct sample enriched in **21*** (mp 155–157 °C, $[\alpha]_D$ +10.6° (*c* 8.3, C_2H_5OH)) and 400 mg of sodium hydroxide in 15 mL of isopropyl alcohol was heated at reflux for 16 h under an atmosphere of nitrogen. The reaction mixture was cooled, made acidic (pH 1) by the careful addition of 3 N hydrochloric acid, and then made basic (pH 9) by the careful addition of 3 N ammonium hydroxide. Pentane (10 mL) and 300 mg of manganese dioxide were added, and the slurry was stirred at room temperature for 20 min under nitrogen. The reaction mixture was poured onto cold water, the layers were separated, and the aqueous layer was extracted with pentane (2 × 10 mL). The combined organic layers were washed with water (5 × 30 mL) and saturated salt solution (30 mL) before drying. The solvent was removed in vacuo and the residue was chromatographed at −25 °C on 2.5 g of Florisil. Elution with pentane (fraction size 50 mL) afforded in fraction 2 21.2 mg of a colorless liquid which was molecularly distilled (60 °C, 0.1 mm) to yield pure **5***, $[\alpha]_D$ −310, $[\alpha]_{578}$ −323, $[\alpha]_{546}$ −377, $[\alpha]_{436}$ −778, and $[\alpha]_{365}$ −1800° (*c* 0.15, *n*-hexane). The CD spectrum was obtained using this sample.

A 100-mg sample of adduct **20***, $[\alpha]_D$ −12.0° (*c* 11.0, C_2H_5OH), when subjected to the identical reaction and workup conditions, gave **5***, $[\alpha]_D$ +54.8, $[\alpha]_{578}$ + 57.7, $[\alpha]_{546}$ +67.5, and $[\alpha]_{436}$ +138° (*c* 10.7, diglyme). This sample was used for some of the kinetic runs.

A 100-mg sample of adduct enriched in **21***, $[\alpha]_D$ +4.30° (*c* 11.4, C_2H_5OH), was subjected to the identical reaction and workup conditions to give a sample of **5***, $[\alpha]_D$ −173, $[\alpha]_{578}$ −182, $[\alpha]_{546}$ −214, and $[\alpha]_{436}$ −445° (*c* 15.0, diglyme). This sample was also used for kinetic runs.

Procedure for Determining the Rate of Racemization of Optically Active 5*. A sample of the optically active **5*** (~30 mg, obtained by hydrolysis–oxidation of a partially resolved *endo*-bornyltriazolinedione adduct) was dissolved in 10.0 mL of purified diglyme (distilled from Na/K alloy) and placed in thoroughly cleaned glass tubes sealed at one end such that about 0.25 mL of solution was present in each tube. These vessels were thoroughly degassed by repeated freeze–thaw cycles under high vacuum (three cycles per tube, using nitrogen to freeze the samples, thawing each sample at less that 10^{-3} mm). The samples were sealed under high vacuum and placed in a constant-temperature bath maintained at the appropriate temperature. After a short equilibration period (about 5 min), a tube was removed and quenched at −78 °C (dry ice–isopropyl alcohol bath) and an accurate timer was started. Tubes were then removed and quenched at the appropriate times. Each tube was opened, the solution was placed in a 0.1-dm polarimeter cell, and the rotation was recorded at 436 nm. Each rotation was plotted, using the previously described rate law, and the method of least squares was applied to evaluate the rate constants.

Procedure for Determining the Rate of Bond Shifting in 5. A small amount (about 30 mg) of 1,2,3,4-tetramethylcyclooctatetraene (obtained by hydrolysis–oxidation of pure phenyltriazolinedione adduct) was dissolved in pentane and transferred to an NMR tube. The pentane was removed under high vacuum and diglyme-d_{14} was distilled onto the sample from Na/K alloy under high vacuum. The solution was degassed by repeated freeze–thaw cycles (liquid nitrogen, three cycles) and sealed under high vacuum. The sample was placed in a constant-temperature bath maintained at the appropriate temperature and after a short equilibration period (about 5 min) removed and quenched at −78 °C (dry ice–isopropyl alcohol bath) and its NMR spectrum was recorded, using a Varian T-60 spectrometer. The methyl region was scanned, using a fully expanded scale, and integrated with respect to an internal standard (benzene), using a planimeter. The data were plotted, using the previously described rate law, and the method of least squares was applied to evaluate the rate constants.

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