Ghatak and S. Chakrabarty, *ibid.*, **41**, 1089 (1976).
(7) R. L. Autrey and P. W. Scullard, *J. Am. Chem. Soc.*, **90**, 4917, 4924 (1968).
(8) J. A. Marshall and D. E. Seitz, *J. Org. Chem.*, **40**, 534 (1975).
(9) M. M. Rogic, J. Vitrone, and M. D. Swerdloff, *J. Am. Chem. Soc.*, **97**, 3848 (1975).
(10) (a) J. San Filippo, Jr., C.-I. Chern, and J. S. Valentine, *J. Org. Chem.*, **41**, 1077 (1976), (b) R. Volkmann, S. Danishefsky, J. Eggler, and D. M. Solomon, *J. Am. Chem. Soc.*, **93**, 5576 (1971), (c) G. Büchi, K. E. Matsumoto, and H. Nishimura, *ibid.*, **93**, 3299 (1971).
(11) (a) B. M. Trost and T. N. Salzmann, *J. Am. Chem. Soc.*, **95**, 6840 (1973); (b) *J. Org. Chem.*, **40**, 148 (1975); (c) B. M. Trost, T. N. Salzmann, and K. Hiroi, *ibid.*, **98**, 4887 (1976).
(12) D. Seebach and M. Teschner, *Tetrahedron Lett.*, 5113 (1973); *Chem. Ber.*, **109**, 1601 (1976).
(13) B. M. Trost and K. Hiroi, *J. Am. Chem. Soc.*, **97**, 6911 (1975).
(14) B. M. Trost and K. Hiroi, *J.Am. Chem. Soc.*, **98**, 4313 (1976).
(15) F. Huet, M. Pellet, and J. M. Conia, *Tetrahedron Lett.*, 3579 (1976); T. Mukaiyma, K. Atsumi, and T. Takeda, *Chem. Lett.*, 1033 (1975).
(16) T. Kumamoto, S. Kobayashi, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **45**, 866 (1972).
(17) Cf. E. Vedejs and D. A. Engler, *Tetrahedron Lett.*, 3487 (1976).
(18) D. Barnard, *J. Chem. Soc.*, 4673 (1957); H. J. Shine, M. Rahman, H. Seeger, and G. S. Wu, *J. Org. Chem.*, **32**, 1901 (1967).
(19) For small scale preparations, we oxidized diphenyl disulfide with 2 equiv of *m*-chloroperbenzoic acid in chloroform at 0 °C to give **4** in 96% yield, mp 41–43 °C. For larger scale preparations, we developed an adaptation of the method of A. J. Backer [*Recl. Trav. Chem. Pays-Bas*, **67**, 894 (1948)] and this procedure is reported in detail in the Experimental Section.
(20) H. O. House, "Modern Synthetic Reactions", W. A. Benjamin, Menlo Park, Calif., 1972, Chapter 6.
(21) The first example of this reaction in these laboratories was performed by K. Hiroi.
(22) Also see B. M. Trost and A. J. Bridges, *J. Am. Chem. Soc.*, **98**, 5017 (1976).
(23) R. Criegee in "Oxidation in Organic Chemistry", Part A, K. Wiberg, Ed., Academic Press, New York, N.Y., 1965, p 277. Also see G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.*, 4426 (1955); D. M. Piatak and E. Caspi, *Chem. Commun.*, 501 (1966); H. B. Henbest, D. N. Jones, and G. P. Slater, *J. Chem. Soc. C*, 756 (1967); J. W. Ellis, *J. Org. Chem.*, **34**, 1154 (1969); G. R. Pettit, C. C. Herald, and J. P. Yardley, *ibid.*, **35**, 1389 (1970); T. Sone, S. Terashima, and S. Yamada, *Synthesis*, 725 (1974).
(24) B. M. Trost and Y. Tamaru, *Tetrahedron Lett.*, 3797 (1975).
(25) J. G. Ll. Jones and B. A. Marples, *J. Chem. Soc. C*, 1188 (1970).
(26) C. G. Overberger, A. Fischman, C. W. Roberts, L. H. Arond, and J. Lal, *J. Am. Chem. Soc.*, **73**, 2540 (1951).
(27) C. Chuit, *Helv. Chim. Acta*, **9**, 267 (1926).
(28) R. H. Manske, *J. Am. Chem. Soc.*, **53**, 1104 (1931).
(29) W. Treibs and H. Reinheckel, *Chem. Ber.*, **87**, 356 (1954).
(30) H. Heymann and L. F. Fieser, *Helv. Chim. Acta*, **35**, 631 (1952).
(31) A. Hassner and I. H. Pomerantz, *J. Org. Chem.*, **27**, 1760 (1962); A. Butenandt, J. Schmidt-Thome, and T. Weitz, *Chem. Ber.*, **72**, 417 (1939).

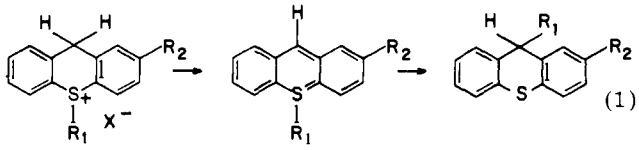
Stereochemistry of the [1,4] Rearrangement of 10-Aryl-10-thiaanthracenes. Asymmetric Induction in the Transfer of Chirality from Sulfur to Carbon with Concomitant Pyramidal Inversion at Sulfur

Cynthia A. Maryanoff, Kathryn S. Hayes, and Kurt Mislow*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received November 1, 1976*

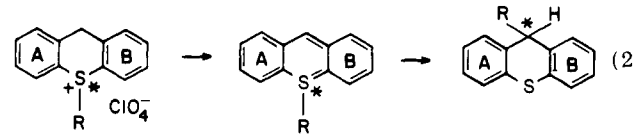
Abstract: Deprotonation of optically active 2-chloro-10-(2,5-xylyl)-10-thioxanthenium perchlorate, resolved via the (+)-camphor-10-sulfonate salt, yielded 2-chloro-10-(2,5-xylyl)-10-thiaanthracene, which rearranged to optically active 2-chloro-9-(2,5-xylyl)-10-thioxanthene. This constitutes the first example of an asymmetric induction in the transfer of chirality from sulfur to carbon accompanying an intramolecular [1,4] rearrangement. The low enantiomeric excess in the product thioxanthene, ca. 7% as determined by ^{1}H NMR, could be ascribed to the configurational instability of the intermediate thiaanthracene, which racemizes about ten times as fast as it rearranges at −15 °C.

Thiaanthracenes (**1**), formed by the deprotonation of thioxanthenium salts (**2**), are unstable compounds which undergo thermal rearrangements to yield the corresponding 9-substituted thioxanthenes (**3**) (eq 1).[1,2] These rearrangements can be formally described as six-electron [1,4] sigmatropic shifts, i.e., as thermal intramolecular rearrangements of cyclic sulfonium ylides.[2]



(1)

The objective of the present work was to determine whether asymmetric induction could be observed in the transfer of chirality from sulfur to carbon in the rearrangement of an unsymmetrically substituted 10-aryl-10-thiaanthracene (eq 2, chiral center starred).[3] Although such inductions had been reported for intramolecular 1,2 shifts,[4,5] no precedent existed for asymmetric inductions in a [1,4] rearrangement.



(2)

A ring ≠ B ring

The system of choice was 2-chloro-10-(2,5-xylyl)-10-thiaanthracene (**1**, R_1 = 2,5-xylyl; R_2 = Cl). Previous work[1,2] had shown that **1** rearranges to 2-chloro-9-(2,5-xylyl)-10-thioxanthene (**3**) intramolecularly (no crossover products were detected) and in high yield (70–80%), and that the rearrangement follows first-order kinetics. The experimental strategy called for resolution of the previously described[1] 2-chloro-10-(2,5-xylyl)-10-thioxanthenium (**2**) perchlorate, and deprotonation of the resolved salt to **1**: assuming pyramidal stability of **1** and **2** on the time scale of the rearrangement **1** → **3**, and stereospecificity in the rearrangement itself, this procedure should lead to enantiomerically enriched **3** and thus to detectable asymmetric induction.

Results and Discussion

Optical Activation of a Thioxanthenium Perchlorate. The chloride of **2**, prepared from the perchlorate by ion exchange

chromatography, was converted in 98% yield to the camphor-10-sulfonate by reaction with silver (+)-camphor-10-sulfonate. Repeated recrystallization of the crude mixture of diastereomeric salts yielded a product, mp 178.5–179.5 °C dec, $[\alpha]^{20}_D$ +27.8° ($CHCl_3$), whose rotation did not change on further recrystallization. The product appeared to be diastereomerically pure as judged by the ^1H NMR spectrum, which showed no resonance doubling of any signals even in the presence of lanthanide shift reagents, and by the noise-decoupled ^{13}C NMR spectrum, which exhibited only the expected 31 signals. The other diastereomer was never isolated, perhaps because the two diastereomers interconvert upon warming in acetone solution, and one crystallizes preferentially (second-order asymmetric transformation).[6] This view gains in plausibility if we consider that the half-life for stereomutation of **2** (by pyramidal inversion at sulfur) is only 3–4 min at 56 °C, assuming an energy barrier for inversion of ca. 25 kcal/mol by analogy with the closely related 9,9-dimethyl-10-phenyl-10-thioxanthenium perchlorate (**4**) ($\Delta G^{\ddagger}$ = 25.4 kcal/mol).[7] The same view also accounts for the observation that in one resolution, the yield of the presumably diastereomerically pure salt was 55% (Experimental Section).

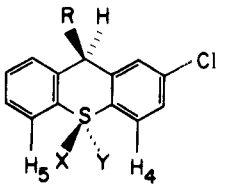
Addition of perchloric acid to a cold methanol–water solution of the diastereomeric salt precipitated **2** perchlorate, which was chemically pure (mp 194–195 °C dec) by IR and ^1H NMR, and was optically active ($[\alpha]^{20}_{400}$ +0.71° (1:4 Me_2SO–CH_3OH)). A solution of this salt at room temperature maintained a constant $[\alpha]^{20}_{400}$ for over 20 h, which gives a lower limit for $\Delta G^{\ddagger}_{rac}$ of 25 kcal/mol.[8] On concentration of a solution of the sulfonium salt at 71 °C, complete loss of optical activity was observed, accompanied by chemical decomposition. Attempts to determine the kinetics of racemization were thus precluded. We were unable to estimate the enantiomeric purity of optically active **2** perchlorate, since ^1H NMR spectra of the racemic perchlorate in $CDCl_3$ failed to show resonance doubling in the presence of the chiral shift reagents $(HFC)_3Eu$ and $(TFC)_3Eu$, or in (+)-2,2,2-trifluoro-1-phenylethanol solution.

Direct determination of diastereomeric and enantiomeric purity of **2** salts thus eluded us throughout this study, and our evidence for diastereomeric and enantiomeric purity in **2** camphorsulfonate and perchlorate therefore remains circumstantial and presumptive in character.[9]

Asymmetric Induction in the Transfer of Chirality from Sulfur to Carbon. Deprotonation of **2** perchlorate, $[\alpha]^{20}_{400}$ +0.71°, at −20 to −15 °C, using a slight deficiency (0.84 molar equiv) of potassium *tert*-butoxide (KOBu(*t*)) in 10:3 toluene–Me_2SO yielded the rearrangement product, **3**, $[\alpha]^{20}_{400}$ −1.64° ($CHCl_3$), in 82% yield (based on KOBu(*t*)). *The optical activity of* **3** *provides unimpeachable evidence for asymmetric induction in the transfer of chirality from sulfur in* **1** *to carbon in* **3**.[10]

Direct determination of the enantiomeric excess (ee) in **3** by NMR techniques proved unsuccessful: the ^1H NMR spectra of racemic **3** failed to show resonance doubling in the presence of $(HFC)_3Eu$, $(TFC)_3Eu$, the corresponding Pr and Yb derivatives, or in (+)-2,2,2-trifluoro-1-phenylethanol solution. On the assumption that our lack of success in differentiating between enantiomers of **2** and **3** by these techniques might be traced to the instability of the association complex between substrate and chiral auxiliary agent, we resorted to structural modifications of **3** which held the promise of alleviating this problem.

Oxidation of racemic **3** with *m*-chloroperbenzoic acid gave a 4:1 mixture of trans:cis sulfoxides **5b:5a.** The peri protons, H-4 and H-5, in both diastereomers are deshielded relative to the remaining aryl protons,[11] and in the presence of shift reagents are cleanly separated in the ^1H NMR spectrum ($CDCl_3$ solution). In the presence of $(TFC)_3Eu$, the signals of the



R = 2,5-xylyl

5a, X = O, Y = electron pair
5b, X = electron pair, Y = O
6, X = Y = O

protons in both isomers are resonance doubled. Since the signals in **5a** fall partially under the peri proton pattern of **5b,** it became necessary to separate the two isomers; this was accomplished by thick layer chromatography, which afforded pure **5b,** uncontaminated by **5a.**

In the presence of 0.59 molar equiv of $(TFC)_3Eu$, the peri proton signals of **5b** appeared as a set of four doublets of equal intensity centered at δ 13.2, 12.5, 12.3, and 11.9 ppm, with $^3J_{HH}$ = 8.5, 7.0, 8.5, and 7.0 Hz, respectively (as deduced by comparison of the 60- and 100-MHz spectra). The four signals may be pairwise assigned to H-4 and H-5, and, within each pair, to the enantiomers of **5b.** If we assume that the two different J values correspond to the two different couplings H-4/H-3 and H-5/H-6, there are only two alternatives: either the two downfield signals originate with one enantiomer of **5b** and the two upfield signals with the other, or the two outside signals originate with one enantiomer and the two inside ones with the other. Since the integrated signal intensities of the two outside signals are significantly different for optically active samples of **5b,** the second one of these alternatives is ruled out. The ee of such samples is then simply estimated from the relationship ee = $|(A - B)/(A + B)|$, where A and B are the integrated intensities of the two outside signals at δ 13.2 and 11.9 ppm. This ee is taken to be the same as the ee of the precursor **3.**

In this way an ee of 7 ± 1% was estimated for **3** with $[\alpha]^{20}_{400}$ −1.64°. A sample of this material, combined with an equal amount of racemic **3** had $[\alpha]^{20}_{400}$ −0.80° and an ee (by NMR) of 3.0 ± 0.5%; this provides a measure of reliability for our method of determining ee.

In contrast to the sulfoxides **5,** the sulfone **6,** prepared by H_2O_2 oxidation of **3,** exhibited no resonance doubling in the presence of chiral shift reagents or in (+)-2,2,2-trifluoro-1-phenylethanol solution.

Pyramidal Inversion at Sulfur in a Thiaanthracene. If one assumes that the starting **2** perchlorate is enantiomerically pure, or nearly so, and that the [1,4] rearrangement **1** → **3** proceeds with complete stereospecificity, as would be expected for this strictly intramolecular rearrangement,[1,2] then one is left with the need to explain the low value of the ee (7%) in the product of rearrangement, **3.**

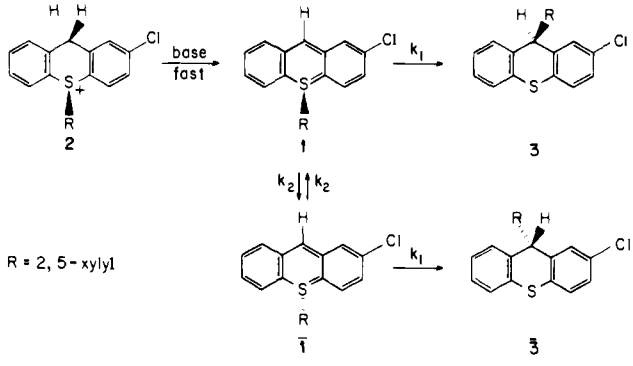
An obvious possibility is that **3** is produced with an initially high ee, but suffers racemization under the basic conditions of the rearrangement.[12] Indeed, when **3,** $[\alpha]^{20}_{400}$ −1.64°, was treated with 0.97 molar equiv of KOBu(*t*) at −15 to −20 °C for 5 min, the produced thioxanthene had $[\alpha]^{20}_{400}$ −1.03°, implying ca. 37% racemization; in support of this conclusion, treatment of racemic **3** under the same conditions, followed by quenching with D_2O/D_2SO_4, resulted in 34 ± 1% incorporation of deuterium in the 9 position. However, whereas treatment of optically active **2** with 1 equiv of 1,8-bis(dimethylamino)naphthalene ("proton sponge") for 4 h yielded **3** with $[\alpha]^{20}_{400}$ −1.56°, reaction of optically active **3** with proton sponge gave no racemization, and reaction of racemic **3** with proton sponge, followed by quenching with D_2O/D_2SO_4, gave *no* deuterium incorporation.[13] Since the optical purity of **3** obtained by deprotonation of **2** with the nonra-

cemizing base 1,8-bis(dimethylamino)naphthalene differs only negligibly from that of the product obtained by deprotonation of **2** with a *deficiency* of KOBu(t), it is reasonable to conclude that the low optical purity in both cases is not primarily due to a process in which **3** is racemized by base subsequent to its formation from **1**.

The remote possibility that the intermediate thiaanthracene **1**, a sulfonium ylide,[1,2] might itself function as a strong base capable of effecting racemization of **3** by proton exchange during the course of the rearrangement was tested in the following experiment. A deficiency (0.84 molar equiv) of KOBu(t) was added to a solution of racemic **2** and a solution of 0.84 molar equiv of active **3**, $[\alpha]^{20}_{400}$ −1.62°, was immediately added to this mixture. The rotation of the recovered **3** was $[\alpha]^{20}_{400}$ −0.90°. Given a rearrangement yield of 80%, the expected $[\alpha]^{20}_{400}$ of −0.90° is in excellent agreement with the observed value, and establishes the fact that **1** does not racemize **3** to a significant extent in the course of the reaction.

Since the starting sulfonium salt, **2** perchlorate, is configurationally stable under the conditions of the rearrangement (see above), the remaining possibility is that the intermediate thiaanthracene **1** racemizes competitively with rearrangement. To test this possibility, active **2**, $[\alpha]^{20}_{400}$ +0.70°, was treated with 0.87 molar equiv of KOBu(t) at −18 °C and held at that temperature for 90 min; the reaction was then quenched (at low temperature) with D_2SO_4/D_2O, the colorless solution was treated with 10% aqueous $HClO_4$, and the perchlorate salt was recovered. The recovered salt had no observable rotation, and had incorporated one deuterium atom in the 9 position. In a similar experiment, when active **2** was treated with 0.84 molar equiv of KOBu(t) and quenched with $HClO_4$ within 4–5 min, the recovered salt was 25% racemized. One is thus forced to the conclusion that the intermediate thiaanthracene **1** suffers racemization under the conditions of the rearrangement.

Scheme I



Kinetics of Pyramidal Inversion. The picture developed in the preceding section is summarized in Scheme I, which shows that **1** formed from **2** (arbitrary absolute configuration) either rearranges to give **3**, with a rate constant k_1, or undergoes pyramidal inversion, with a rate constant k_2, to give the enantiomer, $\bar{\mathbf{1}}$. This in turn can either revert to **1** by pyramidal inversion or rearrange to $\bar{\mathbf{3}}$, the enantiomer of **3**.

Scheme I assumes (a) that the rate of deprotonation of **2** is much greater than the rate of rearrangement,[2] (b) that the conversion of **1** to **3** is irreversible, (c) that any racemization pathways other than pyramidal inversion can be neglected, and (d) that the stereospecificity of the rearrangement is complete, i.e., that the transformations **1** → $\bar{\mathbf{3}}$ and $\bar{\mathbf{1}}$ → **3** are disallowed. These simplifying assumptions lead to kinetic equations 3 and 4, where A and $\bar{A}$ **1** and $\bar{\mathbf{1}}$, respectively.[14]

$$(A + \bar{A})_t = (A + \bar{A})_0 e^{-k_1 t} \quad (3)$$

$$\left[\frac{A - \bar{A}}{A + \bar{A}}\right]_t = \left[\frac{A - \bar{A}}{A + \bar{A}}\right]_0 e^{-2k_2 t} \quad (4)$$

Using the data from an experiment in which **2** was deprotonated in 5:2 toluene-Me_2SO and, after 90 min at −18 °C, quenched to give a 77% recovery of **2** (Experimental Section), eq 3 yields $k_1 = 4.8 \times 10^{-5}$ s^{-1}. From the Eyring equation (assuming a transmission coefficient of unity), $\Delta G^{\ddagger}$ (−18 °C) = 20 kcal/mol, in fair agreement with the previously reported[2] value of $\Delta G^{\ddagger} = 20.7 \pm 0.1$ kcal/mol (which leads, by extrapolation, to $k_1 = 1.3 \times 10^{-5}$ s^{-1} at −18 °C) for the rearrangement of racemic **1** in 9:1 toluene-Me_2SO.

In order to obtain values for k_2, attempts were made at first to determine relative ee values[15] of the optically active thiaanthracene intermediate by direct observation. Circular dichroism was employed to monitor λ_{max} (ca. 515 nm in 10:3 toluene-Me_2SO)[2] at room temperature and at 0 °C; optical rotary dispersion was used to monitor the region above and below λ_{max} (at 550 and 450 nm) at room temperature and at 0 °C. However, in both cases the absorption was so intense that, given the low rotational strength of the monitored transition, no displacement from the baseline could be observed. The desired information was therefore obtained indirectly: aliquots of the reaction mixture were withdrawn at periodic time intervals and quenched with aqueous $HClO_4$, and the recovered **2** perchlorate examined polarimetrically. Since protonation is instantaneous and **2** is conformationally stable, the relative ee of the recovered perchlorate may be taken as equal to the relative ee of **1** at the time of quenching. This method yielded rough values of k_2 ranging from 1.5×10^{-4} s^{-1} to 3.5×10^{-4} s^{-1}, corresponding to $\Delta G^{\ddagger}_{inv}$ (−15 °C) = 19.1–19.5 kcal/mol.[16] The salient conclusion emerging from these kinetic studies is that racemization of thiaanthracene **1** proceeds approximately ten times faster than rearrangement to **3**.[14]

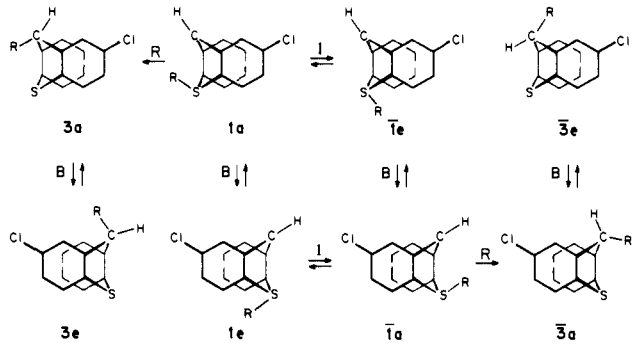
The present study is the first in which a thiabenzene has been observed to undergo pyramidal inversion. Semiempirical MO calculations indicate a barrier to inversion of ca. 43 kcal/mol for *S*-methylthiabenzene[17] and of 35–45 kcal/mol for *S*-phenylthiabenzene.[16b] Experimentally, *lower limits* of 16.8 and 23.7 kcal/mol have been estimated[1] for the inversion barrier at sulfur in 1-isopropyl-2-phenyl-2-thianaphthalene and in 1-pentafluorophenyl-2-methyl-2-thianaphthalene, respectively. That the inversion barrier in **1** is well below the barriers for thiabenzenes and thianaphthalenes may be principally due to the effect of polyaryl substitution at sulfur: when **1** is viewed as a sulfonium ylide,[1,2] the presence of three aryl groups attached to the sulfur center offers greater opportunity for delocalization of the lone pair, thus contributing to a lowering of the transition state energy.[18] A similar effect has been noted for sulfonium ions.[19]

We regard it as highly significant that the inversion barrier in **1** is ca. 6 kcal/mol lower than the barrier in the closely related sulfonium salt **4**.[7] In a previous investigation[20] in which the inversion barrier at sulfur in an ylide was directly compared to that of the corresponding sulfonium ion (in methanol at 50° C), it was found that the enthalpy of activation for the racemization of ethylmethylsulfonium phenacylide, $\Delta H^{\ddagger} = 23.6 \pm 0.2$ kcal/mol (on the assumption that $\Delta S^{\ddagger} \sim 0$), is 5.4 kcal/mol lower than that of ethylmethylphenacylsulfonium perchlorate ($\Delta H^{\ddagger} = 29.0 \pm 0.5$ kcal/mol). If the agreement between the two sets of comparisons is not the result of a fortuitous coincidence, we submit that the barrier lowering in **1** relative to **4** constitutes independent evidence for the description[1,2] of thiaanthracenes as cyclic sulfonium ylides.

We conclude our discussion of the stereochemistry of **1** → **3** by describing some conformational aspects of the rearrangement. We presume that the internal C–S–C angles in **1–3** and the internal C–C(9)–C angles in **2** and **3** are considerably smaller than 120°, and that the ground states of these molecules are therefore folded ("butterfly" conformations).[21] Designating the diastereomeric pseudoaxial and equatorial

forms by suffix letters a and e, respectively, the stereoisomers of **1** and **3** are formally related by pyramidal inversion (*I*), rearrangement (*R*), and boat-to-boat inversion (*B*) as shown in Scheme II.

Scheme II



By analogy with similarly constituted systems (9,10-dihydroanthracenes and structurally related heterocycles),[21,22] molecules of type **1–3** are expected to oscillate rapidly ("flutter") through a planar conformation (process *B*, a ⇄ e) with an energy requirement of no more than ca. 7 kcal/mol. Consequently, the high-energy processes (*R* and *I*, each ca. 20 kcal/mol) dominate the energy profile,[23] and Scheme II effectively collapses to Scheme I. The rearrangement must of course proceed from the a isomer of **1** (or $\bar{1}$), and we note that the a isomer of **3** (or $\bar{3}$) is expected to predominate at equilibrium.[24] Finally, although process *B* occurs independently of the higher energy processes, and with a far higher frequency, it might additionally occur as an event which is intimately coupled to these processes; in that case it would be an inseparable component of *R* and *I*.

Experimental Section[25]

2-Chloro-10-(2,5-xylyl)thioxanthenium Chloride. An ion exchange column was prepared by stirring 300 g of Dowex 2-X8 ion exchange resin (Baker Chemical Co.) with 400 mL of 4% HCl and then with 400 mL of saturated KCl solution. The column was packed and was eluted with distilled water until the eluent no longer gave a positive chloride ion test ($AgNO_3$). After being eluted with ca. 1 L of MeOH, the column was charged with a solution of 9 g of 2-chloro-10-(2,5-xylyl)thioxanthenium (**2**) perchlorate[1] in 50 mL of CH_3CN and, after about 0.5 h, was then eluted with about 300 mL of $MeOH/CH_3CN$. Evaporation of the eluate yielded an oil which was triturated with ether until it solidified. The solid was dried under vacuum to give 6.5–7.0 g of **2** chloride (85–90%), mp 150–165 °C dec. The IR spectrum of this sample did not show the characteristic ClO_4^- band at 1050–1100 cm^{-1}. The crude **2** chloride was used in subsequent reactions without further purification. The ^1H NMR spectrum ($CDCl_3$) featured resonances at δ 2.3 (s, 3 H, $ArCH_3$), 2.77 (s, 3 H, $ArCH_3$), 4.43 and 4.97 (AB q, J = 20 Hz, 2 H, H-9), 6.90 (br s, 1 H, ArH), and 7.47–8.63 (m, 9 H, ArH).

2-Chloro-10-(2,5-xylyl)thioxanthenium Dibenzoyl Hydrogen Tartrate. One gram (2.29 mmol) of the perchlorate salt of **2** was passed through an anion exchange column, and the crude chloride salt was treated with (+)-silver dibenzoyl hydrogen tartrate[26] (2.29 mmol) in 1:2:3 CH_3OH–H_2O–CH_3CN. The silver chloride was removed by filtration of the solution through Celite; concentration of the filtrate gave 1.5 g of oil (94%). Attempts to crystallize this oil from acetonitrile, chloroform, and acetone resulted in purple solutions, indicative of the presence of **1**. The ^1H NMR spectrum of a purple Me_2SO solution exhibited a resonance at δ 5.2 ppm due to the 9 proton of **3**, evidence for the deprotonation of **2** and rearrangement of the resultant **1**.

2-Chloro-10-(2,5-xylyl)-10-thioxanthenium (+)-Camphor-10-sulfonate. Silver oxide (5 g) and (+)-10-camphorsulfonic acid (5 g) were combined in 30 mL of acetonitrile[27] and the mixture was stirred for 20 h at room temperature, under exclusion of light. Filtration of the black suspension through Celite followed by evaporation of the solvent from the filtrate afforded a white solid. Crystallization from acetonitrile/ether yielded needles of silver (+)-camphor-10-sulfonate (5 g, 69%, $[\alpha]^{20}_D$ +14.3° (water), lit.[28] $[\alpha]_D$ +14.56°). A mixture of the silver salt (6.85 g) and 11.5 g of **2** chloride in 250 mL of $CHCl_3$ was stirred for 5 min at room temperature under exclusion of light. The reaction mixture was cooled to −78 °C, filtered through Celite (ca. 3 g of AgCl collected), washed with water, dried, and concentrated to yield 17 g (97%) of an oil. The ^1H NMR spectrum featured resonances at δ 0.82 (s, 3 H, CH_3), 1.13 (s, 3 H, CH_3), 2.23 (s, 3 H, $ArCH_3$), 2.70 (s, 3 H, $ArCH_3$), 1.17–2.87 (m, 7, CH_2, CH), 2.77, 3.57 (AB q, 2 H, J = 16 Hz, CH_2SO_3), 4.27, 4.83 (AB q, 2 H, J = 20 Hz, H-9), 6.75 (br s, 1 H, ArH), 7.18–8.33 (m, 9 H, ArH).

The mixture of diastereomers was fractionally crystallized from acetone/ether. The initial crop had mp 169.0–173.5 °C dec, $[\alpha]^{20}_D$ +22.6°, $[\alpha]^{20}_{365}$ +139° (*c* 1.45, $CHCl_3$). Recrystallization was continued until the product had a constant mp 178.5–179.5 °C dec, $[\alpha]^{20}_D$ +27.8°, $[\alpha]^{20}_{365}$ +165° (*c* 1.26, $CHCl_3$).

Anal. Calcd for $C_{31}H_{33}S_2O_4Cl$: C, 65.41; H, 5.86; S, 11.27; Cl, 6.23. Found: C, 65.45; H, 5.94; S, 11.04; Cl, 6.42.

The noise-decoupled ^{13}C NMR spectrum (in $CDCl_3$) of the final crop featured resonances (downfield from Me_4Si) at 21.1, 21.5, 21.6, 22.3, 25.8, 28.3, 36.8, 43.9, 44.2, 48.2, 48.9, 59.9, 120.8, 122.0, 125.8, 129.9, 130.3, 130.4, 132.2, 133.2, 133.6, 134.8, 134.9, 135.3, 136.0, 139.4, 139.7, 139.8, 141.6, 142.3, 218.0 ppm. ORD curve (CH_3OH): [ϕ] +871, +3770, 0, −3432° at 350, 310 (max), 297, 285 nm, respectively.

Optically Active 2-Chloro-10-(2,5-xylyl)-10-thioxanthenium Perchlorate. A solution of 2-chloro-10-(2,5-xylyl)-10-thioxanthenium camphor-10-sulfonate (0.7 g, $[\alpha]^{20}_D$ +28.0° (*c* 3.49, $CHCl_3$)) in 50 mL of CH_3OH–20 mL of H_2O was cooled in a dry ice–acetone bath until the solution became viscous. $HClO_4$ (70%) (2 mL) was added, followed by 300 mL of H_2O. A precipitate formed immediately. The mixture was stirred for 0.5 h and the solid was collected and washed with water and then with ether. The solid was dried under high vacuum (0.48 g, mp 194–195 °C dec). From the ORD curve a value of $[\alpha]^{20}_{400}$ +0.71° (*c* 1.47, 1:4 Me_2SO–CH_3OH) was obtained. The solution showed no change in rotation upon standing in the ORD cell at room temperature (protected from light) over a period of 20 h. ORD curve (1:4 Me_2SO–CH_3OH): [ϕ] +6.07, +7.69, +8.30, 0, −2.43° at 450, 400, 355 (max), 318, 315 nm, respectively. The IR spectrum showed no carbonyl absorption and had the strong characteristic perchlorate band at 1050–1100 cm^{-1}. The ^1H NMR spectrum (CD_3CN) featured absorptions at δ 2.24 (s, 3 H, $ArCH_3$), 2.73 (s, 3 H, $ArCH_3$), 4.50 (br s, 2 H, 9-H), 6.86 (br s, 1 H, ArH), 7.37–7.98 (m, 9 H, ArH).

Concentration of the ORD sample by heating (at 71 °C) to half its volume resulted in a solution whose ORD curve showed no displacement from the baseline. This inactive sample was added to a volume of water (200–300 mL), and the solution was extracted with ether. Evaporation of the ether layer (after drying) led to an oil whose ^1H NMR spectrum in $CDCl_3$ clearly indicated the presence of 2-chloro-9-(2,5-xylyl)-10-thioxanthene by a singlet at δ 5.1 (H-9), among other unidentified resonances.

2-Chloro-9-(2,5-xylyl)-10-thioxanthene 10-Oxide (5). A solution of 2-chloro-9-(2,5-xylyl)-10-thioxanthene[1] (0.5 g) in 10 mL of CH_2Cl_2 was cooled to 0 °C. *m*-Chloroperbenzoic acid (0.33 g) was added and the reaction mixture was stirred at 0 °C until all reactants became soluble (usually 5 h). Saturated bicarbonate solution was added, and the layers were separated; the organic layer was washed with bicarbonate and then with water, and dried. Evaporation of the solvent gave 0.53 g of a product consisting of a 4:1 mixture of trans:cis sulfoxides. The cis and trans configurations were assigned on the basis of the position of the methine (9-H) proton[24] in the ^1H NMR spectra, the trans isomer having the downfield resonance. The ^1H NMR spectrum ($CDCl_3$) of the mixture featured resonances at δ 1.90 (s, 3 H, cis-$ArCH_3$), 2.37 (s, 3 H, cis-$ArCH_3$), 2.21 (s, 3 H, trans-$ArCH_3$), 2.32 (s, 3 H, trans-$ArCH_3$), 4.97 (br s, 1 H, cis-H-9), 5.90 (br s, 1 H, trans-H-9), 6.73–8.25 (m, 20 H, ArH).

The mixture was chromatographed on a thick layer silica gel plate (PQ4F 2000, Quantum Labs) using three chloroform developments. The UV-absorbing region consisted of two broad bands that were barely separated; collection of the denser lower band afforded an oil. Eventually the oil was crystallized from heptane to afford dense prisms, mp 132.0–133.0 °C. The ^1H NMR spectrum ($CDCl_3$) of the crystals featured resonances at δ 2.20 (s, 3 H, $ArCH_3$), 2.33 (s, 3 H, $ArCH_3$), 5.93 (br s, 1 H, H-9), 6.67–7.58 (m, 8 H, ArH), 7.83–8.33 (m, 2 H, ArH). On the basis of the NMR data[24] the crystals were assigned the trans stereochemistry (**5b**).

Anal. Calcd for $C_{21}H_{17}OSCl$: C, 71.68; H, 4.59; S, 9.11. Found: C, 71.48; H, 4.89; S, 8.96.

For the determination of enantiomeric excess (ee), NMR spectra were recorded on freshly prepared samples (typically 200 mg of **5b**, 300 mg of $(TFC)_3Eu$, 2 mL of dry $CDCl_3$). The integrated intensity of the peri protons H-4 and H-5 was twice that of H-9.

2-Chloro-9-(2,5-xylyl)-10-thioxanthene 10,10-Dioxide (6). A suspension of 2-chloro-9-(2,5-xylyl)-10-thioxanthene[1] (1.0 g) in a mixture of 6 mL of glacial acetic acid and 2.5 mL of 30% H_2O_2 was stirred (protected from light) for 12 days. The mixture was poured into water and extracted with $CHCl_3$. Evaporation of the solvent afforded an oil, which was crystallized from ethanol to give 0.8 g (73%) of dense prisms (mp 162.5-163.5 °C). The ^1H NMR spectrum ($CDCl_3$) featured resonances at δ 1.85 (s, 3 H, $ArCH_3$), 2.38 (s, 3 H, $ArCH_3$), 5.67 (br s, 1 H, 9-H), 6.83-7.67 (m, 8 H, ArH), 8.0-8.33 (m, 2 H, ArH).

Anal. Calcd for $C_{21}H_{17}O_2SCl$: C, 68.38; H, 4.65. Found: C, 67.80; H, 4.72.

Deprotonation Reactions. General Procedure. All reactions were run under nitrogen, and protected from light. The optically active thioxanthenium perchlorate ($[\alpha]^{20}_{400}$ +0.72° (1:4 Me_2SO-CH_3OH)) was dissolved in a mixture of degassed toluene (distilled from sodium) and degassed Me_2SO (distilled from CaH_2). A solution of potassium *tert*-butoxide (sublimed) in Me_2SO was added to the perchlorate solution. The reaction mixtures were initially intensely purple in color, unless otherwise noted. After the reaction mixture became colorless, it was cooled in an ice bath and water was added. The layers were separated and the water layer was washed with $CHCl_3$. The combined organic layers were dried over $MgSO_4$ and concentrated to an oil. Chromatography of the oil on silica gel, eluting with hexane, resulted in a homogeneous oil (the rearrangement product **3**) which could be crystallized from ethanol. The specific rotation of an oil obtained directly from the column and of crystals obtained from this oil proved to be the same. ORD ($CHCl_3$): $[\phi]$ −5.46, 0, +1.67° at 400, 337, 323 nm, respectively. The ^1H NMR ($CDCl_3$) spectrum exhibited resonances at δ 2.17 (s, 3 H, $ArCH_3$), 2.30 (s, 3 H, $ArCH_3$), 5.17 (s, 1 H, H-9), 6.97-7.67 (m, 10 H, ArH).

A. Optically active **2** perchlorate (5 g) in 100 mL of toluene-30 mL of Me_2SO was treated with 1.20 g of potassium *tert*-butoxide in 20 mL of Me_2SO at *room temperature*. Workup after 4 h afforded optically inactive **3** (2.9 g, 80%).

B. Optically active **2** perchlorate (0.70 g) in 50 mL of toluene-15 mL of Me_2SO was cooled to −15 to −20 °C, 0.15 g of potassium *tert*-butoxide in 10 mL of Me_2SO was added, and the bath was removed. Workup after 4 h gave 0.44 g (82%) of an oil (**3**), $[\alpha]^{20}_{400}$ −1.64° (*c* 0.80, $CHCl_3$).

C. Optically active **2** perchlorate (0.7 g, 1.6 mmol) and 0.35 g (1.63 mmol) of 1,8-bis(dimethylamino)naphthalene were combined in 25 mL of Me_2SO-110 mL of toluene at room temperature. The reaction mixture was pale cherry in color. Workup after 4 h gave 0.15 g (28%) of **3**, $[\alpha]^{20}_{400}$ −1.56° (*c* 0.58, $CHCl_3$). Repetition of this reaction using racemic **2** gave the same chemical yield.

D. Optically active **2** perchlorate (1.30 g) was dissolved in 100 mL of toluene-30 mL of Me_2SO and cooled to ca. −18 °C. Potassium *tert*-butoxide (0.29 g) in 10 mL of Me_2SO was added. The reaction mixture was maintained at the initial temperature for 90 min. Cold D_2O/D_2SO_4 was added, followed by $HClO_4$. The mixture was poured onto ice and a precipitate formed. The precipitate was collected, washed with water, then ether, and dried to yield 1.0 g (77%) of recovered **2** perchlorate. The ^1H NMR spectrum (Me_2SO-d_6) showed the incorporation of one deuterium atom: δ 2.33 (s, 3 H, $ArCH_3$), 2.85 (s, 3 H, $ArCH_3$), 4.72 (br s, 1 H, H-9), 7.08 (br s, 1 H, ArH), 7.40-8.40 (m, 9 H, ArH). An ORD sample (*c* 2.0, 1:4 Me_2SO-CH_3OH) gave no observable rotation (the lower limit of observation was ca. $[\alpha]^{20}_{400}$ +0.10°). The usual workup of the rearrangement product yielded 110 mg of **3** after column chromatography; however, the sample was still slightly yellow in color. The $[\alpha]^{20}_{400}$ of the product was −2.85° (*c* 0.33, $CHCl_3$).

E. Optically active **2** perchlorate (0.70 g) in 50 mL of toluene-15 mL of Me_2SO was treated with 0.15 g of potassium *tert*-butoxide in 10 mL of Me_2SO at ca. −18 °C. After 4 min, a 30% $HClO_4$ solution was added; because of the viscosity of the solution, the time elapsed before the solution became colorless was 4-5 min. The reaction mixture was poured into 1 L of ice water and the precipitate was collected by suction filtration, washed with water and ether, and dried to give 0.68 g of recovered **2** perchlorate. The rotation of the collected salt was $[\alpha]^{20}_{400}$ +0.65° (*c* 1.85, 1:4 Me_2SO-CH_3OH).

F. Racemic **2** perchlorate (0.70 g) was dissolved in 50 mL of toluene-15 mL of Me_2SO and cooled to ca. −18 °C; 0.15 g of potassium *tert*-butoxide in 10 mL of Me_2SO was added. *Immediately* after the *tert*-butoxide solution addition was completed, a solution of 0.45 g of active **3** ($[\alpha]^{20}_{400}$ −1.62°, *c* 1.03 ($CHCl_3$)) in 5 mL of toluene was added. After warming to room temperature, the reaction mixture was stirred overnight. The usual workup afforded 0.82 g of **3** with $[\alpha]^{20}_{400}$ −0.90° (*c* 1.66, $CHCl_3$). The expected rotation, $[\alpha]_{exp}$, was calculated as follows. Let *a* = moles limiting reagent (= 0.15/112.2), *b* = fraction of **2** rearranged, i.e., yield (= 0.80), *c* = mol wt of **3** (= 336.9). Then *abc* (0°) + 0.45 (−1.62°) = (*abc* + 0.45)$[\alpha]_{exp}$, whence $[\alpha]_{exp}$ = −0.90°.

Control Experiments on the Product of Rearrangement (3). A. A solution of 0.35 g of 1,8-bis(dimethylamino)naphthalene in 20 mL of toluene was added to a solution of 0.30 g of optically active **3** ($[\alpha]^{20}_{400}$ −1.62° (*c* 1.03, $CHCl_3$)) in 25 mL of Me_2SO-90 mL of toluene. The reaction mixture was stirred overnight at room temperature. After the usual workup, 0.26 g of **3** with $[\alpha]^{20}_{400}$ −1.60° (*c* 0.87, $CHCl_3$) was obtained.

The reaction was repeated as above except that racemic **3** was used and the reaction mixture was quenched with D_2O/D_2SO_4. No D was incorporated (by ^1H NMR).

B. A solution (2.6 mL) of 0.62 g of potassium *tert*-butoxide in 20 mL of Me_2SO was added to a solution of 0.25 g of optically active **3** ($[\alpha]^{20}_{400}$ −1.64° (*c* 0.80, $CHCl_3$)) in 10 mL of toluene-3 mL of Me_2SO, and cooled to ca. −18 °C. After 5 min the reaction mixture was quenched with cold concentrated HCl and worked up in the usual manner. The oil was crystallized from ethanol; the first crop (0.16 g, 64%) had $[\alpha]^{20}_{400}$ −1.03° (*c* 1.07, $CHCl_3$). This result implied 37% racemization.

The reaction was repeated as above except that racemic **3** was employed and the reaction mixture was quenched after 5 min with D_2O/D_2SO_4. Integration of the ^1H NMR spectrum of the crude oil (H-9 at δ 5.1 vs. methyl at δ 2.17 and 2.30; 12:111) implied 35% D incorporation, while that of the crystallized **3** (15:134) implied 33% D incorporation.

Kinetics of Pyramidal Inversion. The general procedure used was as follows. A deficiency (typically 0.8 equiv) of KOBu(*t*) was added to a sample of optically active **2** perchlorate, and after a set period of time the reaction mixture was quenched with aqueous $HClO_4$. The recovered perchlorate was examined polarimetrically, and the rotation of the recovered salt was corrected for the presence of a molar excess (typically 0.2 equiv) of unreacted perchlorate. This correction is only approximate since, in order to compute the fractional decrease in optical purity, the simplifying assumption has to be made that reprotonation of **1** by **2** is a negligible process. To the extent that this approximation does not hold, the calculated values of k_2 are too high, since a factor of $(1 - x)[\alpha]_0$ is subtracted from $[\alpha]_t$, where x = fractional molar equiv of KOBu(*t*).

On this basis, the results described under Deprotonation Reaction E (above) lead to a value of k_2 = ca. 5×10^{-4} s^{-1} and $\Delta G^{\ddagger}_{inv}$ = 19 kcal/mol. Similar values were obtained in the following set of experiments. A solution of 0.450 g of KOBu(*t*) in 25 mL of DMF[29] was added to a solution of 2.10 g of optically active **2** perchlorate in 200 mL of DMF; the addition took approximately 1.25 min. The temperature of the reaction mixture was maintained at −15 °C. Aliquots were taken at regular intervals over a period of 80 min, and quenched with the appropriate quantity (5 or 10 mL, depending on the size of the aliquot) of 10% aqueous $HClO_4$. The perchlorate salts were filtered, washed with ether, dried, and examined on the Cary 60 spectropolarimeter at 420 nm in 1:4 Me_2SO-CH_3OH. Uncorrected rotations fell in the range of α_{obsd} +0.0068 to +0.0030°, with an uncertainty of ±0.0008°. Values of k_2 were computed as described above and in the text, and led to $\Delta G^{\ddagger}_{inv}$ = 19.1-19.5 kcal/mol.

Acknowledgment. We thank the National Science Foundation (CHE74-18161) for support of this work.

References and Notes

(1) (a) B. E. Maryanoff, J. Stackhouse, G. H. Senkler, Jr., and K. Mislow, *J. Am. Chem. Soc.*, **97**, 2718 (1975); (b) G. H. Senkler, Jr., B. E. Maryanoff, J. Stackhouse, *J. D.* Andose, and K. Mislow in "Organic Sulfur Chemistry—Structure, Mechanism and Synthesis", C. J. M. Stirling, Ed., Butterworths, London, 1975, p 157.

(2) F. Ogura, W. D. Hounshell, C. A. Maryanoff, W. J. Richter, and K. Mislow, *J. Am. Chem. Soc.*, **98**, 3615 (1976).

(3) The phrase "asymmetric induction in the transfer of chirality" implies the preservation of all or some of the enantiomeric excess in the transformation

of 1 → 3. The phrase "transfer of chirality" does not by itself express the full meaning of what we intend to convey, since chirality may be taken to refer to an individual molecule, and in that case would be transferred *even in a completely nonstereospecific rearrangement.*

(4) Asymmetric induction in intramolecular transfers of chirality between sulfur and carbon has been demonstrated for allylic [2,3] sigmatropic rearrangements. (a) C → S: P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4869 (1968). (b) S → C: B. M. Trost and R. F. Hammen, *ibid.*, **95**, 962 (1973).

(5) An asymmetric induction in an intramolecular transfer of chirality from sulfur to carbon has been reported for a Pummerer rearrangement: B. Stridsberg and S. Allenmark, *Acta Chem. Scand. Ser. B*, **28**, 591 (1974); **30**, 219 (1976); T. Numata and S. Oae, *Tetrahedron Lett.*, 1337 (1977).

(6) Second-order asymmetric transformations of sulfonium salts have been previously discussed.[4b]

(7) K. K. Andersen, M. Cinquini, and N. E. Papanikolaou, *J. Org. Chem.*, **35**, 706 (1970).

(8) Racemization of a sulfonium salt is an irreversible first-order process, so that $x = a(1 - e^{-k_1 t})$, where a = initial concentration, and x = amount reacted. Assuming a limit of experimental error of 10% (i.e., $x = 0.10$), $k_1 = 1.38 \times 10^{-6}$ s^{-1} and a lower limit of $\Delta G^{\ddagger}$ (20 °C) is 25.0 kcal/mol.

(9) The choice of chiral anions other than camphorsulfonate is severely limited by the sensitivity of **2** to deprotonation. For example, solutions of **2** (+)-dibenzoyl hydrogen tartrate are purple in color and show the presence of the rearrangement product, **3** (Experimental Section). The use of chiral anions of strong acids (e.g., sulfonates) is therefore an essential prerequisite for the resolution.

(10) Sulfur is the only element of chirality in the starting **2** perchlorate. Asymmetric induction by rearrangement of **2** camphorsulfonate would be ambiguous since the anion itself provides a chiral environment which could exert some influence on the direction and magnitude of the induction.

(11) Such deshielding is frequently observed in thioxanthene 10-oxides; for example, cf. S. A. Evans and A. L. Ternay, Jr., *J. Org. Chem.*, **40**, 2993 (1975), and references cited therein.

(12) Optically active 2-dimethylamino-9-methylfluorene is racemized by phenyllithium: G. Wittig, F. Vidal, and E. Bohnert, *Chem. Ber.*, **83**, 359 (1950). Although KOBu(*t*) is a somewhat weaker base, note that **3** is a triphenylmethane with vinylogous sulfur activation.

(13) *cis*- or *trans*-9-methylthioxanthene 10-oxide can be epimerized using KOBu(*t*) or sodium methoxide, but not triethylamine: L. Ens, Ph.D. Thesis, Case Western Reserve University, 1969.

(14) Since a deficiency of KOBu(*t*) was employed, **2** was present in the reaction mixtures throughout the course of the rearrangements. If proton transfer were to occur reversibly between **1** and **2** the calculated values of k_2 would be proportionately decreased (see Experimental Section). The k_2's and energies of activation for the inversion of **1** reported in this paper are therefore the lower limits, the upper limits being k_1 and the energy of activation for rearrangement of **1** to **3**, respectively. In this connection, see also the related case of inversion at nitrogen in partially protonated amines: M. Saunders and F. Yamada, *J. Am. Chem. Soc.*, **85**, 1882 (1963).

(15) The absolute value of the ee is not required for the determination of k_2 since the reaction follows a first-order law (eq 4).

(16) The rate constant for racemization $k_{rac} = 2k_2$, and therefore $\Delta G^{\ddagger}_{rac}$ (cal/mol) = $\Delta G^{\ddagger}_{inv} - 1.37\,T$ (K).

(17) A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, *J. Am. Chem. Soc.*, **93**, 6507 (1971).

(18) Although for steric reasons the 2,5-xylyl ring cannot be coplanar with the thiaanthracene framework in the transition state to inversion, the resulting attenuation of the π overlap with the electron pair on sulfur is not expected to be severe.

(19) D. Darwish and C. E. Scott, *Can. J. Chem.*, **51**, 3647 (1973).

(20) D. Darwish and R. L. Tomilson, *J. Am. Chem. Soc.*, **90**, 5938 (1968); S. J. Campbell and D. Darwish, *Can. J. Chem.*, **52**, 2953 (1974). See also D. M. Roush and C. H. Heathcock, *J. Am. Chem. Soc.*, **99**, 2337 (1977).

(21) For a detailed description of stereoisomerism in folded molecules containing a chiral center, such as **1–3**, cf. the discussion of the stereochemically correspondent 2-methyl-10-(*p*-carboxymethyl)-5,10-dihydroarsacridine: K. Mislow, A. Zimmerman, and J. T. Melillo, *J. Am. Chem. Soc.*, **85**, 594 (1963).

(22) A. K. Chandra, *Tetrahedron*, **19**, 471 (1963); J. Chickos and K. Mislow, *J. Am. Chem. Soc.*, **89**, 4815 (1967), and references cited therein; P. T. Lansbury, *Acc. Chem. Res.*, **2**, 210 (1969); D. M. Wieland and C. G. McCarty, *J. Org. Chem.*, **37**, 4285 (1972).

(23) By the Curtin–Hammett principle; cf. E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, p 151 ff.

(24) A. L. Ternay, Jr., L. Ens, J. Herrmann, and S. Evans, *J. Org. Chem.*, **34**, 940 (1969); A. L. Ternay, Jr., and S. A. Evans, *ibid.*, **39**, 2941 (1974).

(25) Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Unless otherwise noted, ^{1}H NMR spectra were recorded on a Varlan A-60A spectrometer and refer to ca. 10% solutions with tetramethylsilane as an internal reference. The ^{13}C NMR and 100-MHz ^{1}H NMR spectra were recorded on a Varian XL-100 spectrometer, and integrated intensities on this instrument were used to calculate values of enantiomeric excess. Infrared spectra were recorded on a Perkin-Elmer 237B spectrometer. ORD and CD measurements were recorded on a Cary Model 60 spectropolarimeter equipped with a Model 6001 circular dichroism accessory. Specific rotations at 589 and 365 nm were measured on a Perkin-Elmer 141 polarimeter; solution concentrations are given in g/100 mL. Melting points were determined on a Thomas-Hoover apparatus and are corrected. We also note that solutions (or oils and to a lesser extent the crystals) of thioxanthenium salts (**2**), of the rearrangment product (**3**), and of derivatives of **3**, **5**, and **6** used in this study are light sensitive (decomposition to a variety of highly colored products of undetermined nature was observed); all solutions, oils or crystals of the above-mentioned compounds were therefore protected from light as much as possible.

(26) D. M. Coyne, W. E. McEwen, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **78**, 3061 (1956).

(27) Procedure of N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Am. Chem. Soc.*, **81**, 4113 (1959).

(28) W. J. Pope and C. S. Gibson, *J. Chem. Soc.*, **97**, 2211 (1910).

(29) This solvent is of comparable polarity to Me_2SO but has the advantage of maintaining the homogeneity of the reaction mixture at lower temperatures.

A Study of the Mechanism of the Cope Rearrangement[1,2]

Michael J. S. Dewar* and Leslie E. Wade, Jr.

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received July 30, 1975*

Abstract: Kinetic studies are reported for the Cope rearrangements of the 2-phenyl, 3-phenyl, 2-(α-naphthyl), 2-(β-naphthyl), 2,4-diphenyl, and 2,5-diphenyl derivatives of 1,5-hexadiene. The results suggest that the transition state for the reaction is a biradicaloid akin to the 1,4-cyclohexylene biradical.

Although the Cope rearrangement of 1,5-hexadienes was discovered over 30 years ago,[3] and although it has been studied in detail by a number of workers,[4] its mechanism is still not completely understood.

It has been established that the reaction is normally intramolecular,[5] that it involves rearrangement of each allyl group, implying the intervention of intermediates with bonding across the 1,6 positions, and that the preferred conformation of such intermediates is analogous to the "chair" conformation of cyclohexane.[6] It is, however, possible for the reaction to take place via the alternative "boat" conformation,[6] even in the case of 1,5-hexadiene (**1**) itself,[7] and indeed the "boat" rearrangement can take place extremely easily if facilitated by relief of ring strain, as in the degenerate Cope rearrangement of semibullvalene.[8-10]

Cope[3,11] assumed that the reaction takes place in a single step via a cyclic transition state, i.e., that it is a pericyclic process in current terminology,[12] and this view has been commonly accepted. According to it the degenerate rearrangement of **1** would be represented as **1** → **2** → **3**, where **2** is the symmetrical transition state, isoconjugate with benzene and so aromatic.[13] On this basis the preferred chair conformation of **2** can be attributed to an antibonding 1,4 interaction.[13] Similar conclusions follow from orbital correlations between **2** and a pair of allyl radicals[12] or from arguments based on the frontier orbital method.[14]