measures have been thoroughly examined, and, provided certain limitations are recognized, they yield good experimental figures for charge changes in the bond in question[13d,19] in solution reactions. As originally formulated the Leffler approach employed a model reaction with only one major bond change.[20] Since the majority of reactions involve *more* than one major bonding change, it is not surprising that conflicting results have often been obtained concerning advancement of the transition state by application of the simple theory. An explicit experimental test of the Leffler method moreover indicates its usefulness applied to an individual bonding change.[21] Studies on the nature of charge in only one bond in a reaction where more than one bond is changing are unlikely to give a proper description of the transition state.

If the tightness parameter is to be applied to the state of bonding in a transition state, it requires that the reaction be concerted otherwise the reaction is not symmetrical. The Leffler method is applied to *each* bond change in the reaction,[13d,19] and allowing for the negative sign of β_{lg} the Leffler parameter (α)[13d,19] for each changing bond indicates that the forming (η_{nuc}) and breaking (η_{lg}) bond orders are β_{nuc}/β_{eq} and $(1 + \beta_{lg}/\beta_{eq})$, respectively; the total bond order is therefore the sum of these values and is the same as that obtained from the tightness parameter methodology by combining eq 1 and 6 to give eq 9.

$$\tau = \beta_{nuc}/\beta_{eq} + \beta_{lg}/\beta_{eq} + 1 \quad (9)$$

This work confirms that the attack of phenolate anions on phenyl acetates has a concerted mechanism involving no structure on its reaction coordinate resembling that from complete bond formation as found at the corners of the reaction energy surface (Figure 1); it indicates that the transition state has a variable structure over this range. Concerted mechanisms with reaction coordinates passing through structures corresponding to complete bond formation are possible for unsymmetrical acyl group transfers such as those involving amine attack on activated esters;[13c] in these cases the transition state will lie near the edges of the reaction map meeting at the structure corresponding to the tetrahedral intermediate. Concerted mechanisms could also occur with a transition-state structure corresponding to that of the acylium ion.

We are not able to derive spatial information from the polar substituent effects except by inference. Presumably the transition-state geometry will vary as the transition-state structure travels along the tightness diagonal from square planar for the open transition state through some intermediate geometry to tetrahedral for the tight transition state.[22]

Acknowledgment. We thank the Government of Saudi Arabia for support (S.B.). This paper is dedicated to Myron Bender, a friend and teacher, who made inspired contributions to bioorganic chemistry particularly in the field of carbonyl group transfer in solution.

Registry No. 4-Chloro-2-nitrophenyl acetate, 60386-78-9; 4-formylphenyl acetate, 878-00-2; 3-nitrophenyl acetate, 1523-06-4; 4-acetylphenyl acetate, 13031-43-1; 2-nitrophenyl acetate, 610-69-5; 4-nitrophenyl acetate, 830-03-5; 3-chloro-4-nitrophenyl acetate, 89894-10-0; 3,5-dinitrophenyl acetate, 34253-18-4; 2-chloro-4-nitrophenyl acetate, 18855-84-0; 3,4-dinitrophenyl acetate, 10186-94-4; 2,5-dinitrophenyl acetate, 1523-08-6; 2,4-dinitrophenyl acetate, 4232-27-3; 4-chloro-2,6-dinitrophenyl acetate, 118869-96-8; 2,6-dinitrophenyl acetate, 1523-09-7; phenoxide ion, 3229-70-7; 3-chlorophenoxide ion, 18938-14-2; 4-cyanophenoxide ion, 14609-76-8; 4-formylphenoxide ion, 18938-17-5; 2,4,5-trichlorophenoxide ion, 45773-92-0; 2,3,5-trichlorophenoxide ion, 100414-67-3; pentafluorophenoxide ion, 26910-95-2; 4-methoxyphenoxide ion, 29368-59-0; 4-chlorophenoxide ion, 24573-38-4; 2-fluorophenoxide ion, 32376-32-2; 3,4-dichlorophenoxide ion, 45670-76-6; 2-chlorophenoxide ion, 29650-97-3; 2,3-dichlorophenoxide ion, 96541-70-7; 3,4,5-trichlorophenoxide ion, 60154-34-9; 4-nitrophenoxide ion, 14609-74-6.

Supplementary Material Available: Analytical table and figures for Brønsted correlations for attack of substituted phenolate ion on phenyl ester and of phenolate ion on substituted phenyl acetates (5 pages). Ordering information is given on any current masthead page.

(19) Williams, A.; Thea, S. *Chem. Soc. Rev.* (*London*) **1986**, *15*, 125.
(20) Leffler, J. E. *Science* **1953**, *117*, 340.
(21) Hill, S. V.; Thea, S.; Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1983**, 437.

(22) The geometry along the tightness diagonal does not vary for other systems which have been studied by use of the identity rate method (phosphoryl,[9] sulfuryl,[9] hydride,[5a] and methyl[4] group transfer). In all these cases the method of study involved determination of charge development on the leaving or entering atom; such an approach is not indicative of geometry so that we believe that the method developed by Kreevoy and his colleagues is valid for the present case.

Molecules with Twist Bent Bonds. The Synthesis, Properties, and Reactions of *trans*-Bicyclo[4.1.0]hept-3-ene and Certain Methylated Derivatives

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Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received August 19, 1988*

Abstract: *trans*-Bicyclo[4.1.0]hept-3-ene, 7-methyl-*trans*-bicyclo[4.1.0]hept-3-ene, and 7,7-dimethyl-*trans*-bicyclo[4.1.0]hept-3-ene have been synthesized. Comparison of their ease of oxidation with the ease of oxidation of the analogous *cis*-bicyclo[4.1.0]hept-3-enes has been made. Both the thermal and transition-metal complex promoted rearrangements of the *trans*-bicyclo[4.1.0]hept-3-enes have been studied. These systems thermally convert to the *cis*-bicyclo[4.1.0]hept-3-enes above 100 °C and are catalytically rearranged at ambient temperature. Trans to cis isomerization also occurs at ambient temperature under photoinduced single electron transfer conditions.

It has long been recognized that carbon–carbon σ bonds generally exist in one of two basic forms. The first is that which we associate with unstrained carbon–carbon σ bonds. These involve linear overlap of bonding atomic orbitals and result in the electron density of the bonding molecular orbital being symmetrically distributed around the C–C internuclear line. A second type of carbon–carbon σ bond is that traditionally associated with strained carbon–carbon σ bonds such as those found in cyclopropane and

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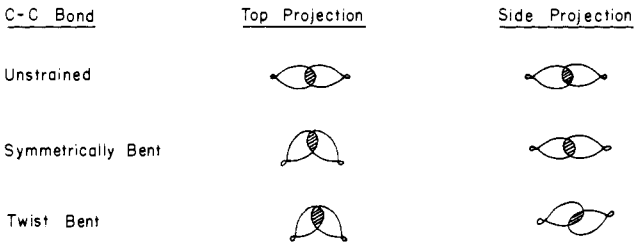
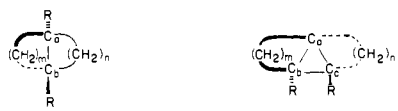


Figure 1. Carbon–carbon σ bonding.

bicyclo[1.1.0]butane. In these bent carbon–carbon σ bonds, the electron density of the bonding molecular orbital deviates from the C–C internuclear line. Projection of the electron density distribution results in displacement from the C–C internuclear line in one plane but not in the orthogonal plane. We chose to describe bonds of this second type as "symmetrically" bent carbon–carbon σ bonds.

Over two decades ago, we first suggested that it should be possible to have a third type of carbon–carbon σ bond, which we defined as a "twist" bent carbon–carbon σ bond.[1] In this third type of bonding picture, the electron density of the bonding molecular orbital is not symmetrically distributed around the C–C internuclear line. In one planar projection, the electron density distribution appears similar to that observed for a symmetrically bent carbon–carbon σ bond. However, in the orthogonal plane, the projection shows the overlapping atomic orbitals, which constitute the bonding molecular orbital as also being displaced from the C–C internuclear line. In this projection, one orbital would be oriented up while the other orbital would be oriented down. This results in an "S" shaped (sinusoidal) electron distribution within the bond. Because these overlapping orbitals are torqued or twisted in opposite directions from the C–C internuclear line, the term twist bent bond is used as a descriptor.

Twist bent carbon–carbon σ bonds should exist in two general types of molecules, one of which can be a subclass of the other. These general classes are constituted of (a) small rings trans-fused to other small rings as exemplified in **1** and (b) small rings cis-fused to two other small rings as catagorized in **2**. For class **1**,

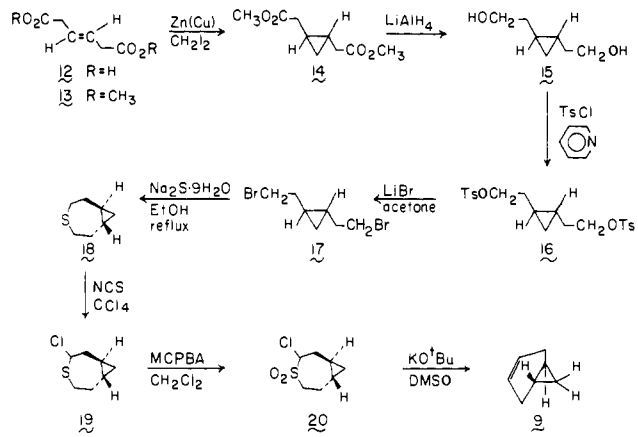


1 **2**

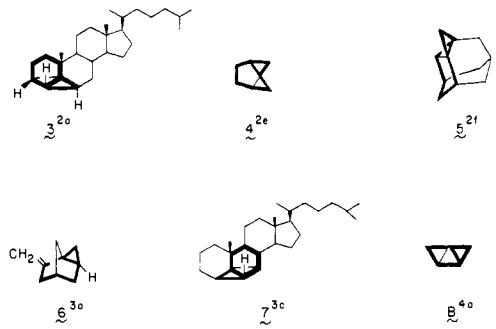
we believe that the increased chemical reactivity associated with the presence of a twist bent bond will appear when $n = 1$ and when m is 5 or less and possibly when $n = 2$ and $m = 2$. For class **2**, increased reactivity should be observed when $n = 1$ and when $m = 4$ or less and possibly when $n = 2$ and $m = 2$. Compounds of type **2** become a subset of type **1** when m or n is 1 and the other is 4 or less.

Several examples of molecules that incorporate **1** as part of a more complex structure have been reported in the literature. In some instances, these molecules were isolable,[2] while in other cases they were proposed as transitory intermediates[2b,3] or as species

Scheme I



that could only be observed at low temperatures.[4] Examples of isolated compounds that should have twist bent carbon–carbon σ bonds are **3–5**, while **6–8** are transitory intermediates that possess



this moiety. The added structural constraints in **3–8** have prevented the use of these molecules for the evaluation of the effect of trans fusion of a small ring to a cyclopropane. As a result, extensive efforts have been devoted to the synthesis of simple *trans*-bicyclo[*n*.1.0]alkanes.[5-8] No evidence exists for the presence of significant strain in the *trans*-bicyclo[6.1.0]nonanes ($n = 6$).[5,6a-e] Studies of *trans*-bicyclo[5.1.0]octanes ($n = 5$)[6] have provided limited evidence for the presence of slightly enhanced reactivity.[6c,f,h] In contrast, the first known example of a simple *trans*-bicyclo[4.1.0]heptane ($n = 4$)[7] was reported to show only limited stability.[8] Our general interest in this area[1,6a,6e,6f] prompted us to undertake a detailed study of the synthesis and reactivity of *trans*-bicyclo[4.1.0]heptane derivatives.[9] This paper provides the

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(6) (a) Gassman, P. G.; Williams, F. J.; Seter, J. *J. Am. Chem. Soc.* **1968**, *90*, 6893. (b) Kirmse, W.; Hase, Ch. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 891. (c) Wiberg, K. B.; de Meijere, A. *Tetrahedron Lett.* **1969**, 519. (d) Ashe, A. J., III *Tetrahedron Lett.* **1969**, 523. (e) Gassman, P. G.; Seter, J.; Williams, F. J. *J. Am. Chem. Soc.* **1971**, *93*, 1673. (f) Gassman, P. G.; Williams, F. J. *J. Am. Chem. Soc.* **1971**, *93*, 2704. (g) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 332. (h) Pirkle, W. H.; Lunsford, W. B. *J. Am. Chem. Soc.* **1972**, *94*, 7201.

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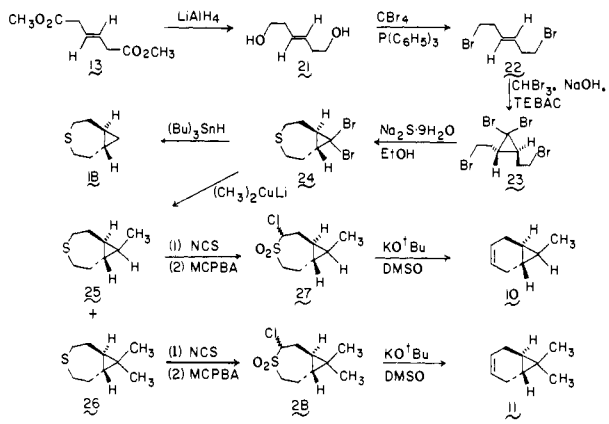
(8) A second derivative of *trans*-bicyclo[4.1.0]heptane has been reported as a nonisolable intermediate. See: Casadevall, E.; Pouet, Y. *Tetrahedron* **1978**, *34*, 1921. For an example of an unsuccessful attempt to prepare a *trans*-bicyclo[4.1.0]hept-3-ene derivative by an acyloin condensation, see: Delbaere, C. U. L.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1974**, 897. See also: Blancou, H.; Casadevall, E. *Tetrahedron* **1976**, *32*, 2907. For an additional unsuccessful approach, see ref 6g.

Scheme II



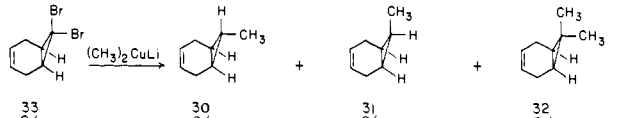
details of the synthesis, properties, and chemical reactivity of *trans*-bicyclo[4.1.0]hept-3-ene (**9**), 7-methyl-*trans*-bicyclo-[4.1.0]hept-3-ene (**10**), and 7,7-dimethyl-*trans*-bicyclo[4.1.0]-hept-3-ene (**11**).

Synthesis of *trans*-Bicyclo[4.1.0]hept-3-enes. As shown in Scheme I, the initial synthesis of *trans*-bicyclo[4.1.0]hept-3-ene started with commercially available *trans*-β-hydromuconic acid (**12**), which was esterified with methanol containing sulfuric acid as a catalyst to give 85% of the dimethyl ester, **13**. Classical Simmons–Smith cyclopropane formation[10] using zinc–copper couple and methylene iodide gave 54% of the trans-disubstituted cyclopropane, **14**. Lithium aluminum hydride reduction of **14** gave a 97% yield of **15**, which on treatment with *p*-toluenesulfonyl chloride in pyridine gave a 96% yield of the ditosylate, **16**. This ditosylate was converted into the corresponding dibromide, **17**, in 97% yield through reflux in acetone containing lithium bromide. High-dilution reaction conditions were necessary in order to achieve a 39% yield of *trans*-4-thiabicyclo[5.1.0]octane (**18**) through the reaction of **17** with sodium sulfide nonahydrate in 95% ethanol. Treatment of **18** with *N*-chlorosuccinimide gave a quantitative yield of crude α-chloro sulfide **19** as a very labile intermediate. Because of the instability of **19**, it was not purified but was immediately oxidized with *m*-chloroperbenzoic acid in methylene chloride to give **20** in 90% yield from **18**. Treatment of **20** with potassium *tert*-butoxide in a classical Ramberg–Bäcklund reaction[11] gave 24% of distilled *trans*-bicyclo[4.1.0]-hept-3-ene (**9**) for an overall yield of 3.4% of **9** from **12**.

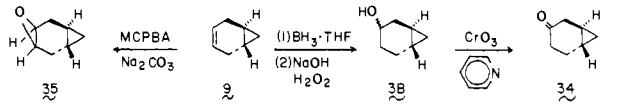
In an attempt to achieve a higher overall yield of **9** and to develop syntheses for both **10** and **11**, the procedures outlined in Scheme II were carried out. Lithium aluminum hydride reduction of **13** gave an 82% yield of **21**, which on treatment with carbon tetrabromide and triphenylphosphine gave 85% of the dibromide, **22**. When **22** was subjected to dibromocarbene addition, the tetrabrominated cyclopropane derivative, **23**, was obtained in 85% yield. This tetrabromide offered a major advantage over the dibromide, **17**, since it reacted with sodium sulfide nonahydrate to form 8,8-dibromo-4-thia-*trans*-bicyclo[5.1.0]octane (**24**) in 68% yield under high-dilution conditions in 95% ethanol. Reductive removal of the bromines from **24** with tri-*n*-butyltin hydride gave a 78% yield of **18**, which was a key intermediate in the synthesis of **9** as outlined in Scheme I. Because of the advantages accrued in the steps leading to **18** as outlined in Scheme II, the overall yield of **9** from **12** was increased to 5.7%.

In order to obtain the 7-methylated derivatives of **9**, **24** was treated with lithium dimethylcuprate to produce a 97% yield of a 53:47 mixture of **25**:**26**. After separation by preparative MPLC, a 41% yield of **25** and a 36% yield of **26** were obtained. Treatment of **25** with 1 equiv of *N*-chlorosuccinimide, followed by oxidation of the intermediate α-chloro sulfide with 2.5 equiv of *m*-chloroperbenzoic acid gave an 82% yield of **27**, which was a mixture of diastereomers due to the presence of both epimers of the chloride. This mixture of diastereomers was not separated. Instead, **27** was treated with 5 equiv of potassium *tert*-butoxide in dimethyl sulfoxide under standard Ramberg–Bäcklund reaction conditions to give 29% of **10**. When **26** was subjected to reaction conditions similar to those used for **25**, **28** was obtained in 90% yield as a mixture of diastereomers. Ramberg–Bäcklund ring contraction of **28** with potassium *tert*-butoxide in dimethyl sulfoxide gave **11** in 45% yield.

The structures of **9**–**11** were established on the basis of both spectral evidence and their facile conversion to their cis isomers (vide post). The ^{1}H NMR spectra of the 4-thia-*trans*-bicyclo-[5.1.0]octanes and the *trans*-bicyclo[4.1.0]hept-3-ene derivatives, which were prepared as part of this study, showed unusual cyclopropane ring anisotropy.[12] For simple cyclopropane derivatives, cyclopropyl methylene protons generally resonate at 0.2–1.0 ppm upfield from cyclopropyl methine protons. For the *trans*-bicyclo[4.1.0]hept-3-ene derivatives prepared as part of this study, this pattern was reversed with the cyclopropyl methine protons resonating at 1.5–2.0 ppm upfield from the cyclopropyl methylene protons. This results in the cyclopropyl methine protons appearing as far as 0.93 ppm upfield from tetramethylsilane. The data are shown in Table I. For comparison purposes, **29** was prepared via the literature procedure.[13] The preparation of **30**–**32**[14] involved



the reaction of lithium dimethylcuprate with 7,7-dibromobicyclo[4.1.0]hept-3-ene (**33**)[15] to yield 65% of a 4:1:10 mixture of **30**:**31**:**32**.[16] Separation of these three products via GLC gave the pure compounds. For **31**, the cyclopropyl protons occurred as overlapping multiplets from δ 0.72 to 0.95 (3 H), and, as a result, the data for **31** is not included in Table I. As can be seen from the comparison of **9**–**11** with **29**, **30**, and **32**, respectively, a major change in ring anisotropy occurs as a result of the trans ring fusion. Not only are the relative positions of the resonance peaks reversed for the methine and methylene protons on the cyclopropane moiety but the chemical shift difference, Δδ, greatly increases. As can be noted for the three *trans*-bicyclo[4.1.0]-hept-3-ene derivatives, which contain both cyclopropyl methine and cyclopropyl methylene protons (**9**, **34**, and **35**), the Δδ values



are 1.77, 1.99 and 1.89, and 1.93 and 0.93. The smallest of these values, 0.93, for the epoxide **35** shows the influence of the epoxide moiety on the cis methine proton. Comparison of **36** and **37**[17,18]

(9) Gassman, P. G.; Bonser, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 667. Gassman, P. G.; Bonser, S. M. *Tetrahedron Lett.* **1983**, *24*, 3431. Gassman, P. G.; Mlinarič-Majerski, K. *J. Org. Chem.* **1986**, *51*, 2397. Gassman, P. G.; Mlinarič-Majerski, K. *Tetrahedron Lett.* **1988**, *29*, 4803.

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(11) Paquette, L. A. *Org. React.* **1977**, *25*, 1.

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(13) Simmons, H. E.; Blanchard, E. P.; Smith, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 1347.

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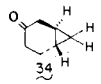
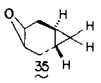
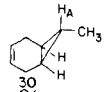
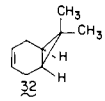
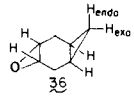
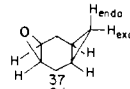
(15) Kumler, W. D.; Boikess, R.; Bruck, R.; Winstein, S. *J. Am. Chem. Soc.* **1964**, *86*, 3126.

(16) Although Paquette and co-workers reported only the formation of **32** (23% yield) from the reaction of lithium dimethylcuprate with **33**, we found that the reaction gave a mixture of **30**–**32** (65% yield).

(17) Aumelas, A.; Casadevall, E.; Casadevall, A. *Tetrahedron* **1978**, *34*, 2481.

(18) Different chemical shifts of δ 0.70[17] and δ 0.55[14] have been reported for the *exo*-methylene proton of **36**.

Table I. ^{1}H NMR Data for Cyclopropyl Methylene and Cyclopropyl Methine Protons of *trans*-Bicyclo[4.1.0]hept-3-ene Derivatives and *cis*-Bicyclo[4.1.0]hept-3-ene Derivatives

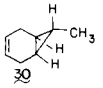
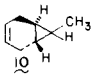
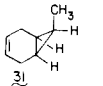
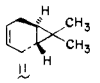
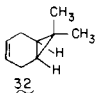
compd	methine protons, δ	methylene protons, δ
 9	−0.50	1.27
 10	−0.46 −0.69	1.60[a]
 11	−0.50	
 34	−0.63 −0.73	1.26
 35	0.07 −0.93	1.00
 29	0.98	0.41
 30	0.57	0.69[a]
 32	0.58	
 36	0.70[b]	−0.40[c] 0.70[d]
 37	0.71[b]	0.62[c] 0.26[d]

[a] Represents the methine proton H_A. [b] Data taken from ref 17. [c] Endo Proton. [d] Exo proton.

shows a deshielding influence of the epoxide ring on the C7 endo proton of **36** of 1.02 ppm relative to **37**. The difference of 1.00 ppm in the two cyclopropyl methine protons of **35** is consistent with the shifts observed for **36** vs **37**. It should be noted that **34** and **35** were prepared from **9** using standard procedures. Epoxidation of **9** with *m*-chloroperbenzoic acid in the presence of sodium carbonate gave a 48% yield of **35**. In order to prepare **34**, **9** was first hydroborated with borane–tetrahydrofuran complex followed by oxidation with hydrogen peroxide under basic conditions to give a 42% yield of the mixed stereoisomers of **38**. Chromium trioxide oxidation of **38** gave **34** in 25% yield.

Oxidation of *trans*-Bicyclo[4.1.0]hept-3-enes. The trans ring fusion incorporated into **9–11** has the effect of severely distorting the skeleton in comparison to the cis ring fused isomers.[19] As a result, a considerable increase might be expected in the energy of the highest occupied molecular orbital (HOMO) of the trans isomers relative to the cis isomers. In order to evaluate these relationships, we chose to study the electrochemical oxidation of these highly strained polycyclic hydrocarbons.[20] As can be seen from Table II, a systematic change occurs in both the *trans*-bicyclo[4.1.0]hept-3-enes and in the *cis*-bicyclo[4.1.0]hept-3-enes as a function of methyl substitution. On average, the addition

Table II. Oxidation Potentials of *trans*-Bicyclo[4.1.0]hept-3-enes, *cis*-Bicyclo[4.1.0]hept-3-enes, and Model Compounds

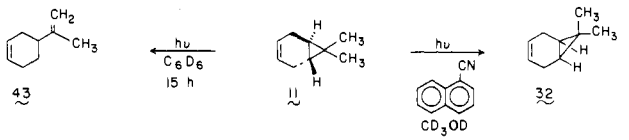
compd	$E_{1/2}$(±0.02 V)	compd	$E_{1/2}$(±0.02 V)
 39	2.07	 29	1.98
 9	1.52	 30	1.83
 10	1.40	 31	1.84
 11	1.34	 32	1.72
 40	2.17		

of a methyl group to the 7-position decreases the $E_{1/2}^{ox}$ by 0.11 V. A systematic change also occurs in the relationship between the trans-fused system and their cis-fused counterparts. The *trans*-bicyclo[4.1.0]hept-3-enes **9–11** are 0.46, 0.43 or 0.44, and 0.38 V more easily oxidized than their cis-fused isomers, respectively. In any comparison of this type, it is important to include simple models. When cyclohexene (**39**) and *cis*-bicyclo[4.1.0]heptane (**40**, norcarane) are compared, the π bond of **39** is oxidized only slightly more readily than the cyclopropane of **40**, since the difference in oxidation potential is only 0.10 V. When both the π bond and the cis-fused cyclopropyl moiety are combined in a single molecule, as in **29**, the $E_{1/2}^{ox}$ drops to 1.98 V. It cannot be determined from this data whether the HOMO of **29** is associated with the double bond or with the cyclopropyl group of **29**, since neither the effect of adding the cyclopropyl ring to **39** on the double bond of **39**, nor the effect of placing a double bond in **40** on the cyclopropyl ring of **40**, can be rigorously determined. What is apparent is that the addition of methyl groups to **29** systematically lowers the $E_{1/2}^{ox}$. For **30** and **31**, the decrease is approximately the same. This argues against a steric effect and supports a purely inductive effect. It seems probable that the methyl groups are too remote to have a significant inductive effect on the π bond. Thus, at least for **30–32** in the cis-fused system, it is likely that the HOMO is associated with the cyclopropyl moiety.

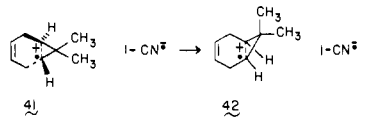
For the *trans*-bicyclo[4.1.0]hept-3-enes, the HOMOs are of much higher energy than for their cis-fused isomers. The same arguments connected with methyl substitution in the cis isomers pertain to the trans-fused derivatives. Thus, while it has not been rigorously determined whether the HOMO of **9** is associated with the double bond or the cyclopropyl moiety, the effect of methyl substitution on the cyclopropyl group of **9** indicates that, at least for **10** and **11**, the HOMO is associated with the twist bent carbon–carbon σ bond of the cyclopropyl moiety. The ease of oxidation of **11** indicates that its HOMO is of comparable energy to the HOMO of the central bond (C1–C4) of bicyclo[1.1.0]-butanes.[20]

The ease with which **11** was electrochemically oxidized suggested that it might be easily susceptible to oxidation by an excited-state photosensitizer in a single electron transfer (SET) process.[21] In order to test this hypothesis, a solution of 1-cyanonaphthalene (1-CN) and **11** in methanol-d_4 was irradiated at 300 nm for 3.5 h. Under these conditions, **11** was converted into **32** in 78% yield. While no other volatile products were formed, it was apparent that some oligomeric materials were produced. Mechanistically, it seems likely that the excited-state 1-CN*, which has an $E_{1/2}$ as an oxidant of 1.84 V, removes an

(19) Dixon, D. A.; Gassman, P. G. *J. Am. Chem. Soc.* **1988**, *110*, 2309.
(20) Gassman, P. G.; Yamaguchi, R. *J. Am. Chem. Soc.* **1979**, *101*, 1308. Gassman, P. G.; Mullins, M. J.; Richtsmeier, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5793. Gassman, P. G.; Mullins, M. J. *Tetrahedron Lett.* **1980**, *21*, 2219. Gassman, P. G.; Yamaguchi, R. *Tetrahedron* **1982**, *38*, 1113.
(21) Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977. Gassman, P. G.; Olson, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 3740. Gassman, P. G.; Hay, B. *J. Am. Chem. Soc.* **1985**, *107*, 4075. Gassman, P. G.; Hay, B. *J. Am. Chem. Soc.* **1986**, *108*, 4227.



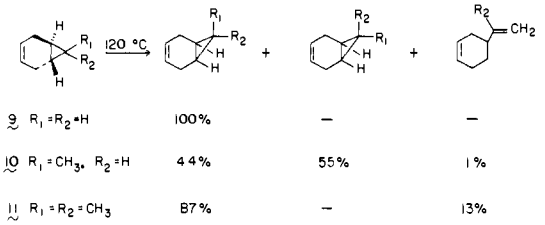
electron from **11** to form the cation-radical–anion-radical pair **41**. Isomerization of **41** to the cis-fused cation-radical–anion-radical



pair **42** could then occur via cleavage of the one-electron bond followed by bond rotation and reformation of the one-electron bond of the cis-fused cation radical of **42**. Back-electron-transfer from the 1-CN anion radical to the cis-fused cation radical would then produce **32** and regenerate the photosensitizer.

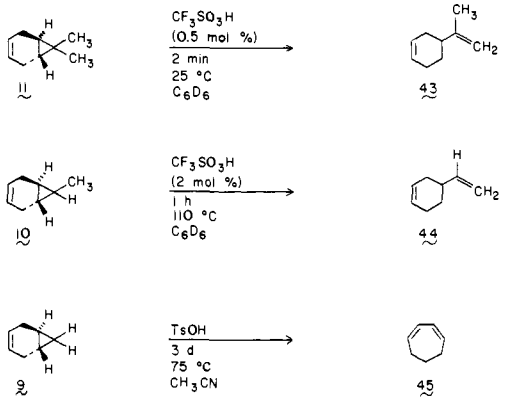
Curiously, the direct irradiation of a benzene-d_6 solution of **11** gave an 88% yield of **43** after 15 h under a 300-nm light source. Solutions of **11** in benzene-d_6 were stable in the dark at 40–45 °C, which was the temperature at which the solution was irradiated.[22] The mechanism of this direct photoprocess is not understood.

Thermal Isomerization of *trans*-Bicyclo[4.1.0]hept-3-enes. All of the *trans*-bicyclo[4.1.0]hept-3-ene derivatives were thermally labile and readily isomerized to their cis isomers above 100 °C. As shown, **9–11** all gave *cis*-bicyclo[4.1.0]hept-3-enes as their



9 $R_1=R_2=H$	100%	–	–
10 $R_1=CH_3$, $R_2=H$	44%	55%	1%
11 $R_1=R_2=CH_3$	87%	–	13%

major thermal isomerization products in 100, 99, and 87% yields, respectively, at 120 °C. In the progression from **9** to **10** to **11**,



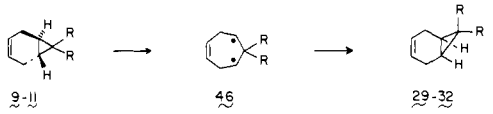
the yields of *trans*-bicyclo[4.1.0]hept-3-ene to *cis*-bicyclo[4.1.0]hept-3-ene decreased slightly with increased methyl substitution. For **11**, it was necessary to include small amounts of Dabco in the reaction mixture in order to prevent the acid-catalyzed rearrangement of **11**. In the presence of Dabco at 130 °C the ratio of **32**:**43** was a constant 93:7. In the absence of Dabco, the ratio varied up to 70:30 for **32**:**43**. This was consistent with the intervention of an acid-catalyzed isomerization of **11** to **43**, which could be achieved in quantitative yield at ambient temperature. In comparison, **10** gave **44** as the only isomeric product plus considerable polymeric material only slowly at 110 °C with acid 4 times more concentrated. For **9**, a more polar solvent was used to facilitate the acid-catalyzed isomerization to **45** (40% conversion after 3 days).

Table III. Kinetics of the Thermal Rearrangement of **9–11** As Determined by ^{1}H NMR Spectroscopy in Toluene-d_8

compd	temp (±3 °C), °C	rate, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{rel} (120 °C)
9	130	$(3.89 \pm 0.05) \times 10^{-5}$			
	120	$(1.19 \pm 0.01) \times 10^{-5}$			
	110	$(4.19 \pm 0.06) \times 10^{-6}$	33.4 ± 1.7	3.5 ± 4.4	1.0
10	130	$(1.50 \pm 0.06) \times 10^{-4}$			
	120	$(4.15 \pm 0.14) \times 10^{-5}$			
	110	$(1.33 \pm 0.01) \times 10^{-5}$	36.4 ± 1.8	13.5 ± 4.7	3.5
11[a]	130	$(3.81 \pm 0.14) \times 10^{-4}$			
	120	$(9.81 \pm 0.79) \times 10^{-5}$			
	110	$(3.27 \pm 0.61) \times 10^{-5}$	36.9 ± 2.8	16.6 ± 7.2	8.2

[a] The kinetics for **11** were complicated by a competing acid-catalyzed process, which introduced problems of replication from run to run. This complication was most prominent at the lower temperatures.

The ease of thermal rearrangement of **9–11** prompted us to examine the kinetics of these isomerizations. The rates of thermal rearrangement, which were determined by ^{1}H NMR, are listed in Table III. The thermodynamic parameters listed are based on the reproducibility of the rates in multiple kinetic runs. If the uncertainty in the thermodynamic parameters is calculated by using the temperature variation of the NMR spectrometer, which was used in the kinetic measurements, much larger error limits are obtained.[23] Thus, the implications of the thermodynamic parameters should not be overinterpreted. As can be seen from Table III, the relative rates increased with methyl substitution at C7. While this rate increase per methyl group was rather small, it was consistent with an additive influence of the methyl groups on the energy of activation. Mechanistically, a process involving homolytic cleavage of the C1–C6 twist bent σ bond is indicated. This would generate **46** as the reactive diradical intermediate, which would reclose to form the *cis*-bicyclo[4.1.0]hept-3-ene skeleton.



The formation of 1% of 4-vinylcyclohexene (**44**) from **10** and 13% of **43** from **11** poses an interesting mechanistic question of whether these ring-opened products result from **46** or whether there is a competing process in which the C1–C7 bond is homolytically cleaved. It seems unlikely that **46** would be prone to rearrangement since relatively few radical rearrangements have been chronicled. Thus, the most likely scenario would involve increased homolytic cleavage of the C1–C7 bond with increased methyl substitution at C7. This implies that in the *trans*-bicyclo[4.1.0]hept-3-enes there is only a small energy difference between the C1–C6 bonding molecular orbital and the C1–C7 bonding molecular orbital. For **11**, where cleavage of the C1–C6 bond generates two secondary radical centers, cleavage of the C1–C7 bond to generate a secondary radical center and a tertiary radical center can successfully compete. This suggests that the difference in energy between the C1–C6 and C1–C7 bonding molecular orbitals may be less than 4 kcal/mol.

Transition-Metal Complex Promoted Rearrangement of *trans*-Bicyclo[4.1.0]hept-3-enes. Our long-standing interest in the transition-metal complex promoted rearrangement of highly strained polycyclic hydrocarbons[24,25] prompted us to examine the behavior of **9–11** in the presence of rhodium(I) catalysts. Scheme III presents the results obtained with bis(μ-chloro)tetra-

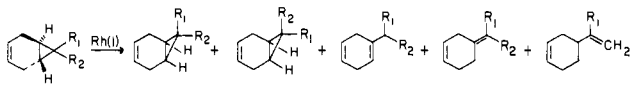
(22) In the presence of acid catalysis, **11** was rapidly converted into **43**. We cannot completely rule out the possibility that, under the photochemical reaction conditions, traces of acid might be generated through some unanticipated process and that this might account for the formation of **43**.

(23) Benson, S. W.; O'Neal, H. E. Kinetic Data on Gas Phase Unimolecular Reactions. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1979**, *No. 21*, 8.

(24) Gassman, P. G.; Williams, F. J. *J. Am. Chem. Soc.* **1972**, *94*, 7733. Gassman, P. G.; Meyer, G. R.; Williams, F. J. *J. Am. Chem. Soc.* **1972**, *94*, 7741. Gassman, P. G.; Atkins, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 7748.

(25) For a leading review, see: Bishop, K. C., III *Chem. Rev.* **1976**, *76*, 461.

Scheme III



$[Rh(CO)_2Cl]_2$					
9 $R_1=R_2=H$	65%	–	–	–	–
10 $R_1=H$, $R_2=CH_3$	9%	5%	11%	9%	3%
11 $R_1=R_2=CH_3$	9%	–	<1%	<1%	58%
$[Rh(COD)Cl]_2$					
9 $R_1=R_2=H$	51%	–	43%	<1%	–
10 $R_1=H$, $R_2=CH_3$	5%	1%	26%	20%	2%
11 $R_1=R_2=CH_3$	3%	–	6%	3%	58%

carbonyldirhodium(I) and bis(μ-chloro)(di-1,5-cyclooctadiene)-dirhodium(I). As can be seen from Scheme III, the yields in these transition-metal complex promoted rearrangements were quite variable, ranging from 94% to 37% material balance. Considerable intractable material was generated in addition to small amounts of what appeared to be an adduct formed from the strained hydrocarbon and the transition-metal complex.[26-28] Of special interest is the ambient temperature isomerization of **9–11** to **29**, **30** and **31**, and **32**, respectively. With both catalysts, the yield of simple trans to cis isomerization decreased with increased methyl substitution at C7. The ratio of other products was determined by the variation in pathways allowed by the methyl substitution at C7. While examples of Lewis acid-catalyzed cis–trans interconversions of specifically substituted cyclopropanes have been reported,[29] the conversion of **9** into **29** with bis(μ-chloro)tetracarbonyldirhodium(I) appears to be the first example of a clean transition-metal complex promoted isomerization of a trans-disubstituted cyclopropane to a cis-disubstituted cyclopropane.[9,30]

Discussion

The experimental results presented above provide a reasonable insight into the reactivity of the *trans*-bicyclo[4.1.0]hept-3-enes. The highly reactive nature of **9–11** is consistent with the bond distortion, which has been calculated by us.[19] As originally postulated,[1] detailed calculations showed that, in the molecular orbital picture of **9**, the C1–C6 bond should have a 6.6° twist as illustrated in **47**.[19] Experimental data obtained for the thermal

47

isomerization of **9** to **29** via **46** indicate an activation energy of 33.9 kcal/mol for the homolytic cleavage of the C1–C6 bond of **9**.[31] The thermal isomerization of a model compound, *cis*-2,3-dimethylcyclopropane (**48**) to *trans*-2,3-dimethylcyclopropane, was shown to have an energy of activation of 61.2 kcal/mol.[32] The difference in energy of activation between these two systems, 27.3 kcal/mol, should reflect the difference in ground-state energies of **9** and **29**, assuming that **46** has no special stabilization or destabilization relative to the diradical formed from **48** and that the only strain energy present in **29** is associated with the cyclopropane. In view of these assumptions, the calculated[19] difference in ground-state energy of 27.1 kcal/mol for **9** vs **29** is in excellent agreement with the value of 27.3 kcal/mol obtained from experimentation.

The electrochemical oxidation of **9–11** vs **29**, **30**, and **31**, and **32** showed $E_{1/2}^{ox}$ differences of 0.46, 0.44 and 0.43, and 0.38 V, respectively. This implies a consistent raising of the HOMO of the *trans*-bicyclo[4.1.0]hept-3-enes relative to the *cis*-bicyclo-[4.1.0]hept-3-enes of an average of 0.43 V or 9.9 kcal/mol. Since the energy difference between **9** and **29** is calculated to be 27.1 kcal/mol,[19] approximately 17 kcal/mol of strain energy must be distributed throughout the other, lower energy, bonding molecular orbitals of **9**. Assuming that the HOMO is associated with the C1–C6 bond, it would seem likely that the C1–C7 and C6–C7 cyclopropyl bonds must also suffer a substantial increase in strain energy.[33] In view of the bond distortions which could occur as part of the incorporation of the cyclopropane moiety into the *trans*-bicyclo[4.1.0]heptyl system, it would not be surprising if bonds of **9** other than the C1–C6 bond might exist with a twist bent orbital overlap.

Experimental Section

Dimethyl *trans*-3-Hexene-1,6-dioate (13). A stirred solution of 300 g (2.08 mol) of *trans*-β-hydromuconic acid (**12**)[35] and 50 mL of concentrated sulfuric acid in 1500 mL of absolute methanol was refluxed for 36 h under a nitrogen atmosphere. The reaction mixture was allowed to cool to room temperature, and the methanol was then removed by rotary evaporation. The residue was poured into 750 mL of saturated aqueous sodium chloride solution and extracted with three 300-mL portions of ether. The combined ethereal extracts were successively washed with saturated aqueous sodium bicarbonate solution, water, and saturated aqueous sodium chloride solution and then dried over anhydrous magnesium sulfate. Filtration and concentration of the filtrate by rotary evaporation afforded 330 g (92%) of crude diester **13** as a pale yellow liquid. Vacuum distillation gave 304 g (85%) of pure dimethyl *trans*-3-hexene-1,6-dioate (**13**) as a clear, colorless liquid, bp 71–74 °C (0.15 mmHg), which crystallized on standing when very pure: ^{1}H NMR ($CDCl_3$/TMS) δ 5.70 (m, 2 H, olefinic), 3.65 (s, 6 H, OCH_3), 3.08 (m, 4 H, allylic); ^{13}C NMR ($CDCl_3$) δ 171.46 (s), 125.57 (d), 51.37 (q), 37.23 (t); IR (neat) 3470, 3005, 2955, 2910, 2845, 1745, 1440, 1415, 1365, 1315, 1300–1150, 1090, 1015, 990, 975, 930, 890, 845 cm^{-1}.

Dimethyl Cyclopropane-*trans*-1,2-diacetate (14). The diester **14** was prepared according to a modified procedure reported by LeGoff.[36] Into a 1-L, three-necked, round-bottomed flask fitted with a condenser, dropping funnel, and overhead stirrer was placed ca. 1.4 mol of the zinc–copper couple (prepared from 20-mesh granular zinc) and 120 mL of anhydrous ether. A solution consisting of 262.48 g (0.98 mol, 79 mL) of diiodomethane and 120.00 g (0.70 mol) of dimethyl *trans*-3-hexene-1,6-dioate (**13**) was added slowly (2–3 h) to the vigorously stirred, refluxing zinc–copper couple/ether mixture. After refluxing for an additional 24-h period, an additional 0.7 mol of zinc–copper couple and 131.24 g (0.49 mol, 39.5 mL) of diiodomethane were added, and refluxing was continued for an additional 24 h. The ethereal solution was decanted from the zinc–copper couple into a flask containing a mixture of ca. 750 mL of 10% hydrochloric acid and ice. The ethereal layer was then separated by means of a separatory funnel and washed with two more portions of ice-cold 10% hydrochloric acid, three times with a large volume of water,[37] and once with a saturated aqueous sodium chloride solution. After drying over anhydrous magnesium sulfate and filtration, the solution was concentrated on a rotary evaporator to give 92.50 g (71%) of crude product as a dark oil. Vacuum distillation yielded 69.45 g (54%) of pure **14** as a clear, colorless liquid, bp 74–77 °C (0.6 mmHg) [lit.[38] bp 87–89 °C (3.0 mmHg)]: ^{1}H NMR ($CDCl_3$/TMS) δ 3.65 (s,

(26) In the rearrangement of **9** by bis(μ-chloro)tetracarbonyldirhodium, a small amount of a yellow-orange powder was obtained, mp 147–149 °C (dec): IR ($CDCl_3$) 3030, 2910, 2840, 2045, 1745, 1730, 1645, 1605, 1435, 1380, 1195, 1155, 1135, 1110, 1070, 995, 955, 815, 780 cm^{-1}. This spectral data can be compared to the starting rhodium(I) complex, which showed sharp bands at 2100, 2090, and 2030 cm^{-1}. It is known that bis(μ-chloro)tetracarbonyldirhodium forms adducts with tetracyclo[3.2.0.0.^{2,7}0^{4,6}]heptane (quadricyclane)[27] and with bicyclo[4.1.0]heptane (**40**).[28] The reaction with **40** produced a dimeric 1:1 adduct, which had carbonyl absorptions at 2050, 1755, and 1735 cm^{-1}. These are very similar to the values that we observed for the adduct of **9** at 2045, 1745, and 1730 cm^{-1}.

(27) Cassar, L.; Halpern, J. *J. Chem. Soc., Chem. Commun.* **1970**, 1082. Gassman, P. G.; Nikora, J. A. *J. Organomet. Chem.* **1975**, *92*, 81.

(28) McQuillin, F. J.; Powell, K. C. *J. Chem. Soc., Dalton Trans.* **1972**, 2129.

(29) Reissig, H.-U.; Böhm, I. *Tetrahedron Lett.* **1983**, *24*, 715.

(30) For a two-step process for the inversion of cyclopropane stereochemistry, which involved the reaction of a cyclopropane with an equivalent amount of bis(benzonitrile)palladium dichloride, see: Rettig, M. F.; Wilcox, D. E.; Fleischer, R. S. *J. Organomet. Chem.* **1981**, *214*, 261.

(31) An energy of activation for the conversion of **9** to **29** of 26.4 kcal/mol was reported by us earlier. Because of the temperatures at which these earlier measurements were made, the error in the data was large. The value of 33.9 kcal/mol is based on data acquired at a more reliable temperature.

(32) Flowers, M. C.; Frey, H. M. *Proc. R. Soc. London, Ser. A.* **1961**, *260*, 424.

(33) This would be consistent with the observed chemical behavior of **9–11**.

(34) Linstead, R. P.; Owen, L. N.; Webb, R. F. *J. Chem. Soc.* **1953**, 1225.

(35) Available from Aldrich Chemical Co., Inc.

(36) LeGoff, E. *J. Org. Chem.* **1964**, *29*, 2048.

(37) During the water washings, a substantial amount of a precipitate forms. The only way to separate the gummy precipitate from the solution was by patiently filtering the solution through a sintered-glass funnel.

(38) Delbaere, C. U. L.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1974**, 879.

6 H, CO_2CH_3), 2.26 (d, 4 H, α-CH_2), 1.20–0.60 (m, 2 H, cyclopropyl methines), 0.60–0.30 (m, 2 H, cyclopropyl methylene protons); ^{13}C NMR ($CDCl_3$) δ 51.08 (q), 37.92 (t), 13.76 (d), 11.08 (t); IR (neat) 3075, 3000, 2955, 2910, 2850, 1745, 1440, 1370, 1305, 1260, 1195, 1175, 1110, 1065, 1015, 860, 840 cm^{-1}.

***trans*-1,2-Bis(2-hydroxyethyl)cyclopropane (15).**[39] A solution containing 61.90 g (0.33 mol) of **14** in 300 mL of anhydrous ether was slowly added to an ice-cold solution of 25.23 g (0.66 mol) of lithium aluminum hydride ($LiAlH_4$) in 1200 mL of anhydrous ether. The mixture was stirred for 3 h at reflux under a nitrogen atmosphere, after which the reaction mixture was cooled to 0–5 °C. Ice water (~3 mL of H_2O/1 g of $LiAlH_4$) was *cautiously* added in order to destroy the excess hydride agent. The white precipitate, which formed upon the addition of the water, was filtered and washed several times with ether. The ethereal filtrate was dried over anhydrous sodium sulfate/potassium carbonate, filtered, and concentrated to afford 36.15 g (83.5%) of crude **15** as a viscous yellow oil. Meanwhile, the dried, precipitated salts were subjected to a Soxhlet extraction for a 24–36-h period. The combined ethereal extracts were dried over anhydrous sodium sulfate/potassium carbonate, filtered, and concentrated to yield an additional 6.80 g (15.7%) of crude product. The total combined crude yield of the diol, **15**, was 42.95 g (99%). Vacuum distillation gave 41.82 g (97%) of pure *trans*-1,2-bis-(2-hydroxyethyl)cyclopropane (**15**) as a clear, colorless, viscous oil, bp 98–100 °C (0.2 mmHg): ^1H NMR ($CDCl_3$/TMS) δ 4.04 (s, 2 H, OH; exchanged with D_2O), 3.65 (dd, 4 H, $-OCH_2-$, J = 4.7 Hz), 2.10–1.70 (m, 2 H), 1.30–0.85 (m, 2 H), 0.75–0.10 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 62.57 (t), 36.32 (t), 15.83 (d), 9.43 (t); IR (neat) 3335, 3065, 2995, 2925, 2870, 1475, 1450, 1433, 1375, 1335, 1263, 1235, 1203, 1148, 1135, 1065, 1043, 1020, 1003, 965, 933, 895, 853, 843, 775, 750 cm^{-1}. Exact mass mol wt. Calcd for $C_7H_{14}O_2$: 130.0994. Found: 130.0995.

***trans*-1,2-Bis[2-(tosyloxy)ethyl]cyclopropane (16).** A solution composed of 27.30 g (0.21 mol) of the diol, **15**, in 150 mL of dry pyridine was placed into a 1-L Erlenmeyer flask, fitted with a magnetic stirring bar. To this stirred, ice-cold solution was added a solution of 99.95 g (0.52 mol) of *p*-toluenesulfonyl chloride in 250 mL of dry pyridine. The reaction mixture was allowed to stir at 0 °C for 0.5 h and then placed in a freezer (−15 °C) overnight. The reaction mixture was poured into ca. 750 mL of ice and 10% aqueous hydrochloric acid, to which concentrated hydrochloric acid was added to pH 3. A semisolid material formed during this process. The aqueous solution was extracted with ether, and the combined ethereal extracts were washed with saturated aqueous sodium bicarbonate solution and saturated aqueous sodium chloride solution and dried over anhydrous magnesium sulfate. Filtration and concentration (rotary evaporation) of the filtrate gave 89.01 g (97%) of the ditosylate, **16**, as a white crystalline solid, mp 59–61 °C. This material was >95% pure (by ^1H NMR analysis) and was used in the next step without further purification.

An analytical sample was obtained upon recrystallization from hexane; mp 63–64 °C: ^1H NMR ($CDCl_3$/TMS) δ 7.54 (AA′BB′, 8 H, Ar), 4.00 (t, 4 H, $TsOCH_2-$), 2.42 (s, 6 H, $ArCH_3$), 1.48 (m, 4 H, $TsOCH_2CH_2-$), 0.65–0.10 (m, 4 H, cyclopropyl methine and methylene protons); ^{13}C NMR ($CDCl_3$) δ 144.57 (s), 133.09 (s), 129.71 (s), 127.71 (s), 70.20 (t), 33.00 (t), 21.47 (q), 14.49 (d), 10.85 (t); IR (KBr) 3060, 2995, 2955, 2935, 2920, 2905, 2850, 1925, 1815, 1610, 1600, 1495, 1465, 1455, 1438, 1430, 1400, 1385, 1355, 1308, 1295, 1275, 1253, 1240, 1223, 1213, 1190, 1175, 1125, 1100, 1065, 1040, 1020, 1005, 973, 930, 900, 880, 865, 845, 815, 780, 760, 735, 705, 655, 580, 570, 550, 500, 485, 420, 385, 365 cm^{-1}. Anal. Calcd for $C_{21}H_{26}O_6S_2$: C, 57.51; H, 5.98. Found: C, 57.37; H, 6.01.

***trans*-1,2-Bis(2-bromoethyl)cyclopropane (17).** The ditosylate, **16** (131.40 g, 0.30 mol), was dissolved in 1 L of acetone. Lithium bromide (260.23 g, 3.0 mol) was added, and the mixture was stirred at reflux for 1.5 h. A precipitate (LiOTs) separated immediately. The acetone was removed by rotary evaporation, and the residue was diluted with water. The organic layer was separated, and the aqueous layer was extracted twice with 30–60 °C petroleum ether. The combined organic extracts were dried (anhydrous magnesium sulfate) and filtered, and the solvent was removed (rotary evaporation) to yield 75.80 g (99%) of the crude dibromide, **17**, as a clear yellow oil. Vacuum distillation afforded 74.43 g (97%) of pure *trans*-1,2-bis(2-bromoethyl)cyclopropane (**17**) as a clear colorless liquid, bp 65–68 °C (0.25 mmHg): ^1H NMR ($CDCl_3$/TMS) δ 3.42 (t, 4 H, $BrCH_2-$), 1.75 (pair of dd, 4 H, $BrCH_2CH_2-$), 0.85–0.20 (m, 4 H, cyclopropyl methine and methylene protons); ^{13}C NMR ($CDCl_3$) δ 36.95 (t), 32.99 (t), 17.20 (d), 11.04 (t); IR (neat) 3070, 3000, 2965, 2928, 2895, 2865, 2835, 1450, 1432, 1355, 1272, 1260, 1213, 1085, 1030, 1005, 940, 880, 855, 845, 755, 740, 632 cm^{-1}. Anal. Calcd for $C_7H_{12}Br_2$: C, 32.84; H, 4.73. Found: C, 33.15; H, 4.76.

(39) Wittig, G.; Wingler, F. *Chem. Ber.* **1964**, *97*, 2139.

4-Thia-*trans*-bicyclo[5.1.0]octane (18). Into a 12-L, four-necked, round-bottomed flask, equipped with an overhead stirrer, reflux condenser, and two 1-L pressure equalizing addition funnels, was placed 8.5 L of 95% ethanol. A solution composed of 40.0 g (0.156 mol) of *trans*-1,2-bis(2-bromoethyl)cyclopropane (**17**) in 1 L of 95% ethanol and a solution composed of 37.5 g (0.156 mol) of sodium sulfide nonahydrate in 1 L of 95% ethanol were added separately and simultaneously to the well-stirred, refluxing solvent over 2.5–3.0 days under a nitrogen atmosphere. The reaction mixture was allowed to reflux an additional 3–5 days. The excess 95% ethanol was distilled at atmospheric pressure in order to concentrate the mixture. Water (1 L) was added to the concentrate (which turned milky white at this point), and this emulsion was extracted three times with 300-mL portions of ether. The combined ethereal extracts were washed with saturated aqueous sodium chloride solution and dried over anhydrous magnesium sulfate. Filtration and concentration of the filtrate afforded 16.40 g (82%) of the crude sulfide, **18**, as a pale yellow oil (pungent sulfide odor). Vacuum distillation gave 7.82 g (39%) of pure 4-thia-*trans*-bicyclo[5.1.0]octane (**18**) as a clear colorless liquid, bp 57–59 °C (2.5–2.6 mmHg).

An analytical sample was obtained by preparative GLC (10% Carbowax 20M Chrom P 60/80) at a column temperature of 160 °C. The material that was collected (10 mg) was then vacuum distilled with a molecular distillation apparatus. GLC analysis of the analytical sample exhibited one peak on a 10% Carbowax 20M Chrom P 60/80 column at 160 °C as well as on a 10% SE-30 column at 120 °C: ^1H NMR ($CDCl_3$/TMS) δ 2.94 (t, 4 H, $-CH_2SCH_2-$), 2.32 (m, 2 H, "exo" methylene protons), 1.06 (m, 2 H, "endo" methylene protons), 0.79 (t, 2 H, methine protons), 0.52 (m, 2 H, cyclopropyl methylene protons); ^{13}C NMR ($CDCl_3$) δ 38.87 (t), 31.47 (t), 19.44 (d), 14.71 (t); IR (neat) 3050, 2980, 2970, 2930, 2905, 2838, 2800, 1458, 1440, 1415, 1353, 1292, 1280, 1260, 1228, 1212, 1200, 1175, 1120, 1100, 1068, 1028, 968, 952, 930, 875, 823, 810, 785, 715, 662, 620 cm^{-1}. Exact mass mol wt. Calcd for $C_7H_{12}S$: 128.0661. Found: 128.0658. Anal. Calcd for $C_7H_{12}S$: C, 65.56; H, 9.44. Found: C, 65.54; H, 9.54.

3-Chloro-4-thia-*trans*-bicyclo[5.1.0]octane 4,4-Dioxide (20). A mixture of 14.60 g (0.114 mol) of 4-thia-*trans*-bicyclo[5.1.0]octane (**18**) and 15.20 g (0.114 mol) of *N*-chlorosuccinimide in 300 mL of carbon tetrachloride was refluxed for 3 h under a nitrogen atmosphere. The reaction mixture was cooled, and the succinimide was removed by filtration. The filtrate was concentrated to give 18.45 g (99.6%) of 3-chloro-4-thia-*trans*-bicyclo[5.1.0]octane (**19**) as an orange oil that discolored on prolonged exposure to air: ^1H NMR ($CDCl_3$/TMS) δ 5.46 (dd, 1 H, CHCl, major isomer) and 5.22 (dd, 1 H, CHCl, minor isomer) in a ratio of 71:29. Because **19** rapidly decomposed on prolonged exposure to air, it was not further characterized and was utilized immediately in the next reaction.

The oil, **19**, was dissolved in 500 mL of methylene chloride and cooled to 0 °C under a nitrogen atmosphere. To this magnetically stirred solution was added 51.77 g (0.300 mol) of *m*-chloroperbenzoic acid in small portions over a 15-min period, and the reaction mixture was allowed to stir at room temperature overnight. After cooling to 0–5 °C, the *m*-chlorobenzoic acid was removed by filtration, and the filtrate was washed with 1 N aqueous sodium hydroxide solution (or saturated aqueous sodium bicarbonate solution), water, and saturated sodium chloride solution. The organic layer was filtered after drying over anhydrous magnesium sulfate and concentrated to afford 20.74 g (94%) of the crude α-chloro sulfone, **20**, as a yellowish semisolid. Chromatography on silica gel, with ethyl acetate as the eluent, gave **20** as a purified oil. The oil was dissolved in ether and cooled to give a 90% yield of pure 3-chloro-4-thia-*trans*-bicyclo[5.1.0]octane 4,4-dioxide (**20**) as small white crystals, mp 72–74 °C.

An analytical sample of **20** was obtained by recrystallizing 100 mg of **20** from ether three times. The epimeric α-chloro sulfones, **20**, were obtained (80.5 mg) as a white, highly crystalline material, mp 75.0–76.5 °C: ^1H NMR ($CDCl_3$/TMS) δ 4.96 (m, 1 H, CHCl), 4.20–3.05 (m, 2 H, $-CH_2SO_2-$), 2.70–2.10 (m, 2 H, "exo" methylene protons), 2.05–1.51 (m, 1 H, "endo" methylene proton), 1.51–0.50 (br m, 5 H, "endo" methylene proton and cyclopropyl methine and methylene protons); ^{13}C NMR ($CDCl_3$) δ 80.69 (C-3), 80.55 (C-3′), 58.69 (C-5′), 56.65 (C-5), 36.51 (C-2′), 36.08 (C-2), 24.07 (C-6′), 22.61 (C-6), 19.95, 17.92, 17.00, 15.20 (two overlapping signals), 14.69. Exact mass mol wt. Calcd for $C_7H_{11}O_2SCl$: 194.0167. Found: 194.0176. Anal. Calcd for $C_7H_{11}O_2SCl$: C, 43.19; H, 5.69. Found: C, 43.17; H, 5.66.

***trans*-Bicyclo[4.1.0]hept-3-ene (9).** To a stirred, ice-cold solution of 4.86 g (25 mmol) of 3-chloro-4-thia-*trans*-bicyclo[5.1.0]octane 4,4-dioxide (**20**) in 20 mL of dimethyl sulfoxide was added, in one portion, 7.0 g (62.5 mmol) of powdered potassium *tert*-butoxide. The mixture was stirred for 30 min at ambient temperature under a nitrogen atmosphere. Water (50 mL) was added to the reaction mixture, and 50 mL of pentane was added. The layers were separated, and the organic layer was washed

with two 30-mL portions of water. The pentane layer was dried (anhydrous sodium sulfate) and filtered, and the solvent was removed to afford a liquid residue. Distillation afforded 0.56 g (24%) of *trans*-bicyclo[4.1.0]hept-3-ene (**9**) as a clear, colorless liquid, bp 45–50 °C (142 mmHg): ^{1}H NMR ($CDCl_3$/TMS) δ 5.92 (m, 2 H, olefinic protons), 2.85–1.85 (br m, 4 H, allylic protons), 1.27 (t, 2 H, cyclopropyl methylene protons), −0.50 (2 H, cyclopropyl methine protons); ^{13}C NMR ($CDCl_3$) δ 132.53 (d, $J_{^{13}C-H}$ = 156.80 Hz), 32.95 (t, $J_{^{13}C-H}$ = 129.35 Hz), 18.42 (t, $J_{^{13}C-H}$ = 160.15 Hz), 16.35 (d, $J_{^{13}C-H}$ = 147.20 Hz); Raman (neat) 3080, 3035, 3010, 2980, 2925, 2860, 1590 (C=C stretch, 0.01), 1440 (0.32), 1415 (0.44), 1275 (0.40), 1255 (0.05), 1200 (0.11), 1170 (0.14), 1125 (0.04), 1070 (0.12), 880 (0.03), 835 (0.05), 790 (0.44), 445 (0.06), 395 (0.49), 345 (0.61) cm^{-1}. Exact mass mol wt. Calcd for C_7H_{10}: 94.0783. Found: 94.0779. Anal. Calcd for C_7H_{10}: C, 89.29; H, 10.71. Found: C, 89.36; H, 10.73.

1,6-Dihydroxy-*trans*-3-hexene (21). A solution of 86.1 g (0.5 mol) of dimethyl *trans*-3-hexene-1,6-dioate in 150 mL of dry ether was slowly added to an ice-cold solution of 38.0 g (1.0 mol) of lithium aluminum hydride in 650 mL of dry ether. The mixture was stirred for 4 h at reflux under a nitrogen atmosphere. The excess of lithium aluminum hydride was destroyed by the careful addition of water. The white precipitate, which formed, was filtered and washed three times with ether (150 mL). The ethereal solution was dried over anhydrous magnesium sulfate and filtered. Concentration of the solution on a rotary evaporator gave 54.5 g (94%) of crude product. Vacuum distillation afforded 47.5 g (82%) of pure **21** as a colorless oil, bp 95–98 °C (0.4 mmHg) [lit.[40] bp 146–148 °C (21 mmHg)]; IR (neat) 3300, 2920, 2860, 1450 (br), 1380, 1045, 970 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.4 (m, 2 H), 4.35 (s, 2 H, −OH), 3.5 (t, 4 H), 2.45–2.0 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 128.8 (d), 61.2 (t), 35.5 (t).

1,6-Dibromo-*trans*-3-hexene (22). A solution of 138 g (0.52 mol) of triphenylphosphine in 250 mL of methylene chloride was added dropwise to a cooled (ice–water) solution of 23.2 g (0.2 mol) of 1,6-dihydroxy-*trans*-3-hexene (**21**) and 180 g (0.54 mol) of carbon tetrabromide in 200 mL of methylene chloride. The mixture was stirred for 15 h at room temperature, the methylene chloride solution was concentrated, and the solution was filtered to remove the triphenylphosphine oxide. The filtrate was passed through a 20-cm silica gel column with hexane as eluent. Concentration on a rotary evaporator and distillation gave 41.1 g (85%) of pure 1,6-dibromo-*trans*-3-hexene (**22**), as a colorless oil, bp 65–67 °C (0.45 mmHg) [lit.[40] bp 87–89 °C (2 mmHg)]; IR (neat) 3040, 3000, 2965, 2920, 2900, 2860, 2825, 1450, 1430, 1270, 1260, 1210, 970, 660, 640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.50 (m, 2 H), 3.35 (t, 4 H), 2.8–2.35 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 129.7 (d), 35.6 (t), 32.2 (t).

3,3-Dibromo-*trans*-1,2-bis(2-bromoethyl)cyclopropane (23). The tetrabromide, **23**, was prepared by phase-transfer catalyzed addition of dibromocarbene to the dibromide, **22**, according to the method of Makosza.[41] To a stirred mixture of 12.1 g (0.05 mol) of 1,6-dibromo-*trans*-3-hexene (**22**), 50.6 g (0.2 mol) of bromoform, 0.2 g of triethylbenzylammonium chloride, 0.8 mL of absolute ethanol, and 25 mL of methylene chloride was added 100 mL of 50% aqueous sodium hydroxide solution during a 1.5-h period. The temperature was kept at 40–45 °C. After the addition of the sodium hydroxide solution, the mixture was stirred at 45 °C for 15 h. The mixture was then poured into 250 mL of water, the organic layer was separated, and the aqueous layer was extracted twice with 30-mL portions of methylene chloride. The combined organic layers were washed with three 50-mL portions of water, three 50-mL portions of dilute hydrochloric acid, and again with water and dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated, the excess bromoform was removed by distillation, and the residue was chromatographed on a 30-cm silica gel column using pentane as eluent. The product was distilled to give 17.7 g (85%) of pure 3,3-dibromo-*trans*-1,2-bis(2-bromoethyl)cyclopropane (**23**), bp 127–129 °C (0.3 mmHg): IR (neat) 3000, 2960, 2930, 2910, 1460, 1260, 1220, 1060, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.5 (t, 4 H), 2.4–1.9 (m, 4 H), 1.7–1.3 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 35.2 (d and t), 34.7 (s), 30.8 (t). Exact mass mol wt. Calcd for $C_7H_{10}Br_4$: 409.7514. Found: 409.7538. Anal. Calcd for $C_7H_{10}Br_4$: C, 20.32; H, 2.44. Found: C, 20.55; H, 2.52.

8,8-Dibromo-4-thia-*trans*-bicyclo[5.1.0]octane (24). A solution of 41.4 g (0.1 mol) of 3,3-dibromo-*trans*-1,2-bis(2-bromoethyl)cyclopropane (**23**) in 1 L of 95% ethanol and a solution of 24.0 g (0.1 mol) of sodium sulfide nonahydrate in 1 L of 95% ethanol were added separately and simultaneously to well-stirred, refluxing, absolute ethanol (12 L) over 2 days under a nitrogen atmosphere. The reaction mixture was allowed to reflux an additional 4 days. The ethanol was removed by distillation at atmospheric pressure through a 20-cm Vigreaux column. Water (2 L) was added to the concentrate, and this mixture was then extracted four times with 250-mL portions of petroleum ether. The combined organic extracts were washed with saturated aqueous sodium chloride solution and dried over anhydrous magnesium sulfate. Filtration and concentration of the filtrate afforded 23.5 g (82%) of the crude sulfide, **24**, as a solid material. Recrystallization from 5% ethyl acetate in hexane afforded 19.5 g (68%) of the pure sulfide, **24**, as white crystals. An analytical sample was prepared by recrystallization from pentane, mp 72–73 °C: IR (KBr) 2960, 2940, 2920, 2860, 1450, 1420, 1290, 1270, 1250, 1185, 1070, 920, 830, 750, 725, 655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.9 (t, 4 H), 2.7–2.3 (m, 2 H), 1.8–1.1 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 38.6 (d), 38.3 (s), 36.3 (t), 30.4 (t). Exact mass mol wt. Calcd for $C_7H_{10}Br_2S$: 283.8869. Found: 283.8866. Anal. Calcd for $C_7H_{10}Br_2S$: C, 29.39; H, 3.53. Found: C, 29.62; H, 3.56.

8-Methyl-4-thia-*trans*-bicyclo[5.1.0]octane (25) and 8,8-Dimethyl-4-thia-*trans*-bicyclo[5.1.0]octane (26). To a stirred suspension of 19.98 g (104 mmol) of cuprous iodide was added dropwise 118 mL (208 mmol) of a 1.76 M solution of methyllithium in ether at −15 °C under a nitrogen atmosphere.[42] After 0.5 h at −15 °C, the reaction mixture was cooled to −30 °C, and 3.0 g (10.4 mmol) of the dibromo sulfide, **24**, in 20 mL of dry ether was added slowly. The reaction mixture was maintained at −30 °C for 5 days with occasional shaking. The mixture was then poured into cold saturated aqueous ammonium chloride solution, which was made alkaline with ammonium hydroxide. Following this, 50 mL of ether was added. The organic layer was separated and washed three times with saturated aqueous ammonium chloride/ammonium hydroxide solution, water, and saturated aqueous sodium chloride solution and dried over anhydrous magnesium sulfate. Filtration, followed by evaporation of the solvent, gave 1.58 g (97.5%) of crude product, which consisted of a mixture of the methyl-substituted sulfide, **25**, and the dimethyl-substituted sulfide, **26**, in the ratio of 53:47 (GLC, OV-101, 150 °C). The sulfides **25** and **26** were separated by MPLC (Lobar, RP-8 column) using 35% water in acetonitrile as eluent. The yield of the pure products was 1.21 g (77%). Analytical samples of **25** and **26** were prepared by an additional chromatography on MPLC (Lobar, Si-60 column) using 2% ethyl acetate in hexane as eluent, followed by distillation in a Kugelrohr apparatus.

Sulfide 25: distillation temperature 40 °C (0.15 mmHg); IR (neat) 3000, 2945, 2910, 2840, 1450, 1420, 1390, 1265, 1115, 1105, 1065, 955, 930, 880, 860 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.0 (t, 2 H), 2.95 (t, 2 H), 2.6–1.9 (m, 2 H), 1.65–0.9 (m, 2 H), 1.12 (d, 3 H), 0.9–0.2 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 38.87 (t), 38.55 (t), 31.32 (t), 27.68 (d), 27.08 (t), 24.69 (d), 21.52 (d), 13.76 (q). Exact mass mol wt. Calcd for $C_8H_{14}S$: 142.0816. Found: 142.0812. Anal. Calcd for $C_8H_{14}S$: C, 67.54; H, 9.92. Found: C, 67.48; H, 9.95.

Sulfide 26: distillation temperature 45 °C (0.15 mmHg); IR (neat) 3000, 2965, 2950, 2920, 2860, 2820, 1465, 1425, 1385, 1295, 1270, 1140, 1090, 1025, 975, 950, 860 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.9 (t, 4 H), 2.45–1.85 (m, 2 H), 1.5–1.0 (m, 2 H), 1.05 (s, 6 H), 0.65–0.25 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 38.72 (t), 32.55 (d), 28.25 (t), 25.94 (s), 21.70 (q). Exact mass mol wt. Calcd for $C_9H_{16}S$: 156.0973. Found: 156.0985. Anal. Calcd for $C_9H_{16}S$: C, 69.17; H, 10.32. Found: C, 68.98; H, 10.27.

3-Chloro-4-thia-8,8-dimethyl-*trans*-bicyclo[5.1.0]octane 4,4-Dioxide (28). A mixture of 1.92 g (12 mmol) of the sulfide **26** and 1.64 g (12 mmol) of *N*-chlorosuccinimide in 45 mL of carbon tetrachloride was refluxed for 3 h under a nitrogen atmosphere. The reaction mixture was cooled, and the succinimide was removed by filtration. The carbon tetrachloride was evaporated to give a quantitative yield of a dark yellow oil. This oil was dissolved immediately in 40 mL of methylene chloride and cooled to 0 °C, and 5.34 g (31 mmol) of 85% *m*-chloroperbenzoic acid was added with stirring. The reaction mixture was stirred at room temperature for 24 h. After cooling, the precipitated *m*-chlorobenzoic acid was removed by filtration, and the filtrate was then washed with two portions of 1 M aqueous sodium hydroxide solution and saturated aqueous sodium chloride solution. The filtrate was dried over anhydrous magnesium sulfate. After filtration, the solvent was removed to give 2.65 g of product as a colorless oil. The product was crystallized from a mixture of ether/pentane (1:5) to yield 2.4 g (90%) of small white crystals, mp 106–109 °C: IR (KBr) 3020, 2980, 2960, 2950, 2925, 2860, 1470, 1420, 1325, 1315, 1295, 1160, 1125, 825, 675 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.95 (m, 1 H), 4.15–3.65 (m, 1 H), 3.4–3.0 (m, 1 H), 2.6–0.5 (m, 6 H), 1.14 (s, 3 H), 1.13 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 80.18 (d), 56.67 (t), 33.20 (t), 32.51 (d), 27.12 (d), 26.74 (s), 21.45 (q), 21.02 (q), 19.37 (t). Exact mass mol wt. Calcd for $C_9H_{15}O_2SCl$: 222.0481. Found: 222.0467. Anal. Calcd for $C_9H_{15}O_2SCl$: C, 48.53; H, 6.79. Found: C, 48.34; H, 6.87.

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3-Chloro-4-thia-8-methyl-*trans*-bicyclo[5.1.0]octane 4,4-Dioxide (27). The α-chloro sulfone, **27**, was prepared according to the procedure used for the preparation of the sulfone, **28**. From 1.75 g (12 mmol) of **25**, was obtained, after recrystallization, 2.05 g (82%) of an epimeric mixture of α-chloro sulfones, **27**, as small white crystals, mp 87–95 °C: IR (KBr) 3000, 2950, 2930, 2865, 1455, 1420, 1320, 1290, 1140, 1120, 680, 500 cm^{-1}; ^1H NMR (C_6D_6) δ 4.62 (m, 1 H), 3.6–3.1 (m, 2 H), 3.0–2.45 (m, 2 H), 2.1–1.35 (m, 2 H), 1.35–0.4 (m, 3 H), 0.8 (br s, 3 H); ^{13}C NMR (major isomer; C_6D_6) δ 80.47 (d), 56.91 (t), 32.20 (t), 27.91 (d), 22.94 (t), 22.58 (d), 19.90 (d), 13.68 (q). Exact mass mol wt. Calcd for $C_8H_{13}O_2SCl$: 208.0325. Found: 208.0323. Anal. Calcd for $C_8H_{13}O_2SCl$: C, 46.04; H, 6.28. Found: C, 46.22; H, 6.40.

7,7-Dimethyl-*trans*-bicyclo[4.1.0]hept-3-ene (11). To a stirred, ice-cold solution of 0.5 g (2.24 mmol) of 3-chloro-4-thia-8,8-dimethyl-*trans*-bicyclo[5.1.0]octane 4,4-dioxide (**28**) in 5 mL of dimethyl sulfoxide was added, in small portions, 1.26 g (11 mmol) of powdered potassium *tert*-butoxide. The mixture was stirred for 20 min at ambient temperature under a nitrogen atmosphere, and 20 mL of pentane was added. The reaction mixture was poured into 50 mL of water, and the organic layer was separated. The aqueous layer was extracted twice with 20-mL portions of pentane. The combined pentane extracts were washed twice with water and saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered, and the solvent was evaporated to give 0.135 g (49%) of crude product. The product was distilled (bulb to bulb, 0.05 mmHg) to yield 0.125 mg (45%) of **11**: IR (neat) 3020, 2970, 2910, 2840, 1595, 1380, 1045 cm^{-1}; ^1H NMR (C_6D_6) δ 5.96 (s, 2 H), 2.55 (dd, 2 H), 2.0 (m, 2 H), 1.1 (s, 6 H), −0.5 (m, 2 H); ^{13}C NMR (C_6D_6) δ 131.61 (d), 32.49 (s), 31.76 (t), 30.99 (d), 23.24 (q). Exact mass mol wt. Calcd for C_9H_{14}: 122.1095. Found: 122.1096. Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.54. Found: C, 88.27; H, 11.52.

7-Methyl-*trans*-bicyclo[4.1.0]hept-3-ene (10). 7-Methyl-*trans*-bicyclo[4.1.0]hept-3-ene was prepared according to the procedure used for the preparation of the *trans*-bicyclo[4.1.0]alkene **11**. From 0.5 g (2.4 mmol) of 3-chloro-4-thia-8-methyl-*trans*-bicyclo[5.1.0]octane 4,4-dioxide (**27**) was obtained 77 mg (29%) of crude **10**. The product was distilled (bulb to bulb, 0.05 mmHg) to yield 53 mg (20%) of **10**: IR (neat) 3020, 2960, 2910, 2850, 1595, 1440, 1100, 1040 cm^{-1}; ^1H NMR (C_6D_6) δ 5.9 (s, 2 H), 2.55 (m, 2 H), 2.00 (m, 2 H), 1.6 (q, 1 H), 1.05 (d, 3 H), −0.46 (m, 1 H), −0.69 (m, 1 H); ^{13}C NMR (C_6D_6) δ 132.81 (d), 132.44 (d), 33.57 (t), 30.60 (t), 26.88 (d), 25.90 (d), 22.45 (d), 16.13 (q). Exact mass mol wt. Calcd for C_8H_{12}: 108.0939. Found: 108.0931. Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.82; H, 11.24.

4-Thia-*trans*-bicyclo[5.1.0]octane (18). Tri-*n*-butyltin hydride (72.67 g, 0.25 mol) was added dropwise to a solution of 23.8 g (0.083 mol) of the dibromo sulfide, **24**, in 50 mL of benzene at 0 °C. The reaction mixture was stirred at room temperature for 3 days. The benzene was removed by distillation in vacuo through a 12-cm Vigreaux column at 27 °C (10 mmHg), and the product was distilled from the remaining fraction at 45 °C (0.45 mmHg). The yield was 8.33 g (78%) of pure 4-thia-*trans*-bicyclo[5.1.0]octane (**18**). The spectroscopic data was identical with that reported above for **18**.

Preparation of *exo*-7-Methyl-*cis*-bicyclo[4.1.0]hept-3-ene (30), *endo*-7-Methyl-*cis*-bicyclo[4.1.0]hept-3-ene (31), and 7,7-Dimethyl-*cis*-bicyclo[4.1.0]hept-3-ene (32). To a stirred suspension of 28.56 g (0.15 mol) of cuprous iodide was added dropwise 200 mL (0.3 mol) of a 1.5 M solution of methyllithium in ether at −15 °C under a nitrogen atmosphere. After 0.5 h at −15 °C, the reaction mixture was cooled to −30 °C, and 3.8 g (0.015 mol) of *cis*-7,7-dibromonorcar-3-ene (**33**)[15] in 20 mL of dry ether was added slowly. The reaction mixture was maintained at −30 °C for 4 days with occasional shaking. The mixture was then poured into cold saturated aqueous ammonium chloride/ammonium hydroxide solution and 50 mL of ether was added. The organic layer was separated and washed with aqueous ammonium chloride/ammonium hydroxide solution, water, and saturated aqueous sodium chloride solution and dried over anhydrous magnesium sulfate. Filtration, followed by evaporation of the solvent gave a mixture of crude products (1.6 g). Chromatography on silica gel with petroleum ether as the eluent gave 1.11 g (65%) of a mixture of three products in a 4:1:10 ratio (according to capillary GLC, OV-101, 50 °C). The products were separated by preparative GLC on an SE-30 column at 135 °C. The main product was 7,7-dimethyl-*cis*-bicyclo[4.1.0]hept-3-ene (**32**):[14] IR (neat) 3030, 3000, 2940, 2875, 2815, 1435, 1380, 690, 650 cm^{-1}; ^1H NMR (C_6D_6) δ 5.51 (s, 2 H), 2.28 (dd, 2 H), 1.88 (d, 2 H), 0.99 (s, 3 H), 0.86 (s, 3 H), 0.58 (d, 2 H); ^{13}C NMR (C_6D_6) δ 125.14 (d), 28.58 (q), 20.17 (t), 17.44 (d), 17.07 (s), 13.52 (q).

The other two products (in 4:1 ratio) were the 7-methyl-*cis*-bicyclo[4.1.0]hept-3-enes (**30** and **31**, respectively).

***exo*-7-Methyl-*cis*-bicyclo[4.1.0]hept-3-ene (30):** IR (neat) 3030, 3010, 2960, 2900, 2840, 1470, 1445, 1390, 1350, 1230, 1220, 1085, 1050, 995 cm^{-1}; ^1H NMR (C_6D_6) δ 5.43 (s, 2 H), 2.36–2.12 (m, 4 H), 0.99 (d, 3 H), 0.69 (q, 1 H), 0.57 (br s, 2 H); ^{13}C NMR (C_6D_6) δ 124.17 (d), 23.82 (t), 18.40 (q), 18.13 (d), 14.20 (d). Exact mass mol wt. Calcd for C_8H_{12}: 108.0939. Found: 108.0939. Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.80; H, 11.04.

***endo*-7-Methyl-*cis*-bicyclo[4.1.0]hept-3-ene (31):** IR (CCl_4) 3020, 2960, 2900, 2870, 2830, 1430, 1125, 1085 cm^{-1}; ^1H NMR (C_6D_6) δ 5.52 (s, 2 H), 2.27 (dd, 2 H), 1.86 (d, 2 H), 0.95–0.72 (m, 3 H), 0.84 (d, 3 H); ^{13}C NMR (C_6D_6) δ 125.61 (d), 19.67 (t), 12.10 (q), 9.10 (d), 6.71 (d). Exact mass mol wt. Calcd for C_8H_{12}: 108.0939. Found: 108.0939. Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.89; H, 11.12.

***trans*-Bicyclo[4.1.0]hept-3-ene Oxide (35).** To an ice-cooled suspension of 340 mg (3.2 mmol) of sodium carbonate and 150 mg (1.6 mmol) of *trans*-bicyclo[4.1.0]hept-3-ene (**9**) in methylene chloride (10 mL) was added dropwise a solution of *m*-chloroperbenzoic acid (487 mg, 2.4 mmol) in methylene chloride (5 mL). The reaction mixture was stirred for 3 h at ambient temperature, and the reaction progress was followed by GLC (OV-101, 90–120 °C). After the starting material had reacted, the reaction mixture was filtered and the filtrate was washed with water, aqueous sodium sulfite solution, and brine prior to drying. Filtration followed by evaporation afforded 84.5 mg (48%) of **35**. An analytical sample was obtained by preparative GLC (glass-column, Carbowax 20 M, with 2% KOH; 115 °C):[43] IR (neat) 3060, 2990, 2910, 2850, 1440, 1025, 920, 850, 800 cm^{-1}; ^1H NMR (C_6D_6) δ 3.18 (m, 1 H), 2.87 (ddd, 1 H), 2.52 (dd, 1 H), 2.25 (m, 1 H), 1.55 (dd, 1 H), 1.20–0.95 (m, 3 H), 0.07 (m, 1 H), −0.93 (m, 1 H); ^{13}C NMR (C_6D_6) δ 57.04 (d), 55.91 (d), 31.21 (t), 30.76 (t), 19.82 (t), 18.47 (d), 9.72 (d). Exact mass mol wt. Calcd for $C_7H_{10}O$: 110.0731. Found: 110.0730.

***trans*-Bicyclo[4.1.0]heptan-3-ols (38).** To a solution of **9** (150 mg, 1.6 mmol) in dry tetrahydrofuran (10 mL), a 1 M solution of borane–tetrahydrofuran complex (1.6 mL) was added under nitrogen atmosphere, and the resulting mixture was stirred for 1.5 h at room temperature. Water (1 mL) was then added, followed by aqueous 10% sodium hydroxide (3.5 mL) and 30% hydrogen peroxide (3.5 mL). The reaction mixture was stirred for 10 h at room temperature, poured into 50 mL of water, and extracted four times with ether. The organic extracts were dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated to give a residue (75 mg, 42%) of the two stereoisomers of **38**: IR (neat) 3350, 3050, 2920, 2855, 1050 cm^{-1}; ^1H NMR (C_6D_6) δ 4.1–0.7 (m, 20 H), −0.4, to −1.1 (m, 4 H); ^{13}C NMR (C_6D_6) δ 74.43, 70.22, 41.18, 40.56, 40.17, 37.70, 31.11, 28.86, 22.09, 21.44, 21.00, 19.42, 18.41, 15.55. Exact mass mol wt. Calcd for $C_7H_{12}O$: 112.0888. Found: 112.0895.[43]

***trans*-Bicyclo[4.1.0]heptan-3-one (34).** Chromium trioxide (0.5 g, 5.5 mmol) was added in small portions, with stirring, to 5 mL of pyridine. After 1 min, the red anhydride turned to a yellow solid. The temperature was kept below 30 °C. The chromium trioxide–pyridine complex solution was stirred for 15 min at room temperature, and the alcohol **38** (70 mg, 0.62 mmol) was added. The reaction mixture was stirred for 2 h at room temperature, poured into 50 mL of water, and extracted with ether. The ethereal extracts were washed three times with brine and dried over anhydrous magnesium sulfate. Filtration, followed by evaporation of the solvent, afforded 35 mg (51%) of the crude product. Chromatography of the crude product on silica gel with 30% ether in pentane as eluent gave 17 mg (25%) of the ketone **34** as a colorless oil: IR (neat) 3075, 2940, 2880, 1725, 1450, 800 cm^{-1}; ^1H NMR (C_6D_6) δ 2.95–0.50 (m, 6 H), 1.26 (t, 2 H), −0.63 (m, 1 H), −0.73 (m, 1 H); ^{13}C NMR (C_6D_6) δ 209.90 (s), 48.68 (t), 43.24 (t), 29.23 (t), 24.50 (t), 20.19 (d), 18.81 (d). Exact mass mol wt. Calcd for $C_7H_{10}O$: 110.0731. Found: 110.0730.[43]

Electrochemical Oxidation of *trans*- and *cis*-Bicyclo[4.1.0]hept-3-enes 9–11 and 29–32. Oxidation half-wave potentials ($E_{1/2}$) for compounds **9–11** and **29–32** versus a standard calomel electrode (SCE) were determined by single-sweep cyclic voltammetry on a Princeton Applied Research Model 174 polarographic analyzer equipped with a stationary platinum microelectrode. All measurements were made in high-purity acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte. The concentrations of the hydrocarbons were 10^{-3} M, and the scan rate was 100 mV/s. Each reported half-wave potential is an average of at least three runs.

Generalized Photochemical Experiment. A solution of 12.2 mg (0.1 mmol) of 7,7-dimethyl-*trans*-bicyclo[4.1.0]hept-3-ene (**11**) in 0.4 mL of methanol-d_4 and 7.6 mg (0.05 mmol) of 1-cyanonaphthalene was placed in an NMR tube and irradiated in a Rayonet photochemical reactor with 16 300-nm light sources. The progress of the reaction was followed by ^1H NMR spectroscopy. When the starting material was completely reacted, 8.5 mg of *n*-decane was added to the solution in order to obtain

(43) Due to the very small quantities of material available and the extensive spectroscopic and chemical data desired from these compounds, elemental analyses were not obtained on **34** and **35**. We were unable to obtain a satisfactory elemental analysis on **38**.

a GLC yield (capillary OV-101, 45 °C).

Reaction of 11 with Triflic Acid. 7,7-Dimethyl-*trans*-bicyclo[4.1.0]-hept-3-ene (**11**) (12.2 mg, 0.1 mmol) was dissolved in 0.4 mL of benzene-d_6 in an NMR tube. To this solution was added 0.075 mg (5×10^{-4} mmol) of triflic acid.[44] The progress of the reaction was followed by ^{1}H NMR spectroscopy. According to the ^{1}H NMR spectrum, **11** rearranged quantitatively to **43** in 2 min.

Reaction of 10 with Triflic Acid. 7-Methyl-*trans*-bicyclo[4.1.0]hept-3-ene (**10**) (10.8 mg, 0.1 mmol) was dissolved in 0.4 mL of benzene-d_6, and 2 mol % of triflic acid was added. The sample was heated at 110 °C. The progress of the isomerization was followed by ^{1}H NMR spectroscopy. According to the ^{1}H NMR spectral data, within 1 h all of the *trans*-olefin **10** rearranged to **44** and to an unidentified polymeric material.

Reaction of 9 with *p*-Toluenesulfonic Acid. *trans*-Bicyclo[4.1.0]-hept-3-ene (**9**) (12 mg, 0.13 mmol) and *p*-toluenesulfonic acid (1.6 mg, 0.008 mmol) in 0.5 mL of acetonitrile-d_3 were placed in an NMR tube and heated to 75 °C. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. After 3 days at 75 °C, most of **9** remained, with only 40% being converted to 1,3-cycloheptadiene.

Thermal Isomerization of 9–11. The rate of thermal isomerization was measured by ^{1}H NMR spectroscopy in toluene-d_8 using a Varian HFT-80 spectrometer. The rates were determined by measuring the decrease in concentration of the starting substrate. The spectra were recorded at appropriate time intervals for at least 3 half-lives to give linear pseudo-first-order rate data. The disappearance of substrate was followed by integration of the olefinic proton signals relative to the methyl signal of the internal standard, *p*-nitroanisole. Approximately 0.08–0.10 mmol of olefins and 0.04–0.05 mmol of *p*-nitroanisole were dissolved in 0.5 mL of toluene-d_8 in a base-washed NMR tube. Pseudo-first-order rate constants were obtained from a least-squares treatment. The ratio of products was determined by integration of olefinic protons in the ^{1}H NMR spectra recorded on a 300-MHz NMR spectrometer.

Reaction of *trans*-Bicyclo[4.1.0]hept-3-ene (9) with Bis(μ-chloro)-tetracarbonyldirhodium. To a solution of 54.6 mg (0.58 mmol) of *trans*-bicyclo[4.1.0]hept-3-ene (**9**) in 0.3 mL of chloroform-*d* was added, in one portion, 24 mg (9.6 mol %) of bis(μ-chloro)tetracarbonyldirhodium. An instantaneous reaction was observed. After a few minutes, the volatiles were vacuum transferred, and 30.2 mg of cyclooctene was added as an internal standard. GLC analysis indicated a 65% yield of *cis*-bicyclo[4.1.0]hept-3-ene (**29**). The formation of **29** as the product was readily established by its ^{1}H NMR analysis.

The residue remaining after vacuum transfer was triturated with a small volume of 30–60 °C petroleum ether and filtered. The yellow-orange powder[26] melted with decomposition at 147–149 °C: IR ($CDCl_3$) 3030, 2910, 2840, 2045 ($\nu_{CO\ acyl}$), 1745 and 1730 ($\nu_{CO\ acyl}$), 1645, 1605, 1435, 1380, 1195, 1155, 1135, 1110, 1070, 995, 955, 815, 780 cm^{-1}.

Reaction of 7-Methyl-*trans*-bicyclo[4.1.0]hept-3-ene (10) with Bis(μ-chloro)tetracarbonyldirhodium. To a solution of 45.4 mg (0.42 mmol) of the olefin **10** in 0.4 mL of benzene-d_6 was added 8.7 mg (5 mol %) of bis(μ-chloro)tetracarbonyldirhodium in one portion at room temperature. The reaction was followed by ^{1}H NMR. After 48 h at room temperature, all starting material had reacted to give a mixture of products. The mixture was vacuum transferred (0.05 mmHg), and 24.0 mg of *n*-decane was added as an internal standard. The overall GLC yield of the product mixture was 17.5 mg (39%). The residue (33 mg) was a yellow-orange solid material. The structures of the rearranged products were established by comparison of their spectra with those of authentic samples prepared in our laboratory (vide post).

Reaction of 7,7-Dimethyl-*trans*-bicyclo[4.1.0]hept-3-ene (11) with Bis(μ-chloro)tetracarbonyldirhodium. To a solution of 56.5 mg (0.46 mmol) of **11** in 0.4 mL of benzene-d_6 was added 8.96 mg (5 mol %) of bis(μ-chloro)tetracarbonyldirhodium in one portion at room temperature. After standing for 14 h at room temperature, all starting material had reacted to give a mixture of products. The mixture was vacuum transferred (0.05 mmHg), and 27 mg of *n*-decane was added as an internal standard. The residue (18.06 mg) was a yellow-orange solid material. The overall GLC yield of the product mixture was 38.4 mg (68%).

Reaction of *trans*-Bicyclo[4.1.0]hept-3-ene (9) with Bis(μ-chloro)(di-1,5-cyclooctadiene)dirhodium. To a solution of 105.4 mg (1.12 mmol) of *trans*-bicyclo[4.1.0]hept-3-ene (**9**) in 0.4 mL of deuteriochloroform was added 13.3 mg (0.027 mmol, 2.4 mol %) of bis(μ-chloro)(di-1,5-cyclooctadiene)dirhodium. After 15–30 min at room temperature, the volatiles were vacuum transferred, and 49.2 mg of cyclooctene was added as an internal standard. A 94% yield of *cis*-bicyclo[4.1.0]hept-3-ene (**29**) and 1-methylcyclohexa-1,4-diene was obtained in a ratio of 54.5 to 45.5 respectively (GLC analysis, 10% SE-30 column, 70 °C; ^{1}H NMR analysis). Also, by ^{1}H NMR analysis, 4-methylenecyclohexene was formed in ≤1% yield. The ^{1}H NMR spectra of the products were identical with those obtained on material independently synthesized by alternate routes.

Reaction of 7-Methyl-*trans*-bicyclo[4.1.0]hept-3-ene (10) with Bis(μ-chloro)(di-1,5-cyclooctadiene)dirhodium. To a solution of 27 mg (0.25 mmol) of **10** in 0.4 mL of benzene-d_6 was added 6.1 mg (5 mol %) of bis(μ-chloro)(di-1,5-cyclooctadiene)dirhodium in one portion at room temperature. After the solution stood for 5 h at room temperature, all starting material had reacted to give a mixture of products. The mixture was vacuum transferred (0.05 mmHg), and 20 mg of *n*-decane was added as an internal standard. The residue (8.8 mg) was a dark yellow material. The overall GLC yield of the product mixture was 14.8 mg (55%).

Reaction of 7,7-Dimethyl-*trans*-bicyclo[4.1.0]hept-3-ene (11) with Bis(μ-chloro)(di-1,5-cyclooctadiene)dirhodium. To a solution of 84.5 mg (0.69 mmol) of **11** in 0.4 mL of benzene-d_6 was added 17.0 mg (5 mol %) of bis(μ-chloro)(di-1,5-cyclooctadiene)dirhodium in one portion at room temperature. After the solution stood for 1.5 h at room temperature, all of the starting material had reacted to give a mixture of products. The mixture was vacuum transferred (0.05 mmHg), and 34 mg of *n*-decane was added as an internal standard. The overall GLC yield of the product mixture was 60.2 mg (71%), and the residue (20.5 mg) was a dark yellow polymeric material. The structures of the rearranged products were established by comparison of their spectra with those of authentic samples.

Control **Experiments.** It was demonstrated that the products of the thermal and transition-metal complex promoted rearrangements of **9–11** were stable to the reaction conditions.

1-Methylcyclohexa-1,4-diene.[45] A modification of the procedure reported by Benkeser et al.[45] was utilized in the synthesis of 1-methylcyclohexa-1,4-diene. Over a period of 1 h, 17 g (0.74 mol) of sodium metal was added to a solution of 13.8 g (0.15 mol) of toluene in 37.5 g (0.75 mol) of ethanol, 300 mL of liquid ammonia, and 40 mL of anhydrous ether. After 1.5 h the metal was gone. The ammonia was allowed to evaporate (overnight) before water was cautiously added in order to hydrolyze the residue. The aqueous layer was extracted with ether several times. The combined ethereal extracts were dried (anhydrous sodium sulfate/potassium carbonate), filtered, and concentrated (atmospheric distillation) to afford 11.8 g (84%) of crude diene. Atmospheric pressure distillation through a 12-cm Vigreaux column yielded 8.95 g (63%) of pure 1-methylcyclohexa-1,4-diene as a clear colorless liquid, bp 115–116 °C (760 mmHg) [lit.[45] bp 115.5–116 °C (760 mmHg)]: ^{1}H NMR ($CDCl_3$/TMS) δ 5.68 (s, 2 H, olefinic protons), 5.39 (br s, 1 H, olefinic proton), 2.59 (s, 4 H, doubly allylic protons), 1.65 (s, 3 H, methyl protons).

Ethyl-1,4-cyclohexadiene and isopropyl-1,4-cyclohexadiene were prepared by Birch reduction of ethylbenzene and isopropylbenzene, respectively.[45]

4-Ethylidenecyclohexene was prepared according to the method of Salomon,[46] which involved reduction of (1-phenylethyl)trimethylsilane with lithium in liquid ammonia, followed by protodesilylation with aqueous hydrochloric acid in tetrahydrofuran–methanol.

4-Isopropenylcyclohexene (43) and 4-isopropylidenecyclohexene were prepared by alkylation of methyl 3-cyclohexenecarboxylate with methyllithium followed by dehydration of the resulting alcohol in dimethyl sulfoxide at 180 °C. The mixture of olefins was separated by preparative GLC (SE-30, 120 °C). The spectroscopic data for **43** were identical with those published,[47] and the spectral data of the other olefin were consistent with the structure of 4-isopropylidenecyclohexene: IR (neat) 3025, 2970, 2910, 2840, 1650, 1435, 1370, 1240 cm^{-1}; ^{1}H NMR (C_6D_6) δ 5.8–5.6 (m, 2 H), 2.7 (br s, 2 H), 2.3 (t, 2 H), 2.05–1.95 (m, 2 H), 1.62 (s, 3 H), 1.55 (s, 3 H) [lit.[48] bp 155–158 °C].

1-[((2-Nitrophenyl)seleno)methyl]-3-cyclohexene. A solution of 250 mg (2.23 mmol) of 1-(hydroxymethyl)-3-cyclohexene in 12 mL of dry tetrahydrofuran was treated with 708 mg (3.12 mmol) of *o*-nitrophenyl selenocyanate[49] and 631 mg (3.12 mmol, 0.78 mL) of tri-*n*-butylphosphine. After the solution was stirred for 15 h at room temperature, the solvent was removed. The crude residue was chromatographed (75 g silica gel, 2:5 ethyl acetate/hexanes) to give 650 mg (98%) of the desired product as a yellow oil. An analytical sample was obtained by

(44) The triflic acid was added in 1,1,2-trichlorotrifluoroethane solution (50 μL). The solution was prepared by dissolving 15 mg of triflic acid in 10 mL of 1,1,2-trichlorotrifluoroethane.

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molecular distillation at 0.05 mmHg: ^{1}H NMR ($CDCl_3$/TMS) δ 8.25 (m, 1 H, ArH), 7.50 (m, 2 H, ArH), 7.28 (m, 1 H, ArH), 5.64 (d, 2 H, olefinic protons, J = 2 Hz), 2.89 (d, 2 H, CH_2SeAr, J = 6 Hz), 2.45-1.70 (br m, 6 H, cyclohexenyl methylene protons), 1.42 (m, 1 H, methine proton); ^{13}C NMR ($CDCl_3$) δ 133.32, 129.05, 126.90, 126.31, 125.44, 125.10, 32.97, 32.80, 32.14, 29.07, 24.62; IR (neat) 3020 (olefinic CH), 2960, 2920, 2840 (aliphatic CH), 1655 (olefinic CC), 1590 (Ar), 1565, 1515 ($ArNO_2$), 1450, 1435, 1330 ($ArNO_2$), 1305, 1250, 1230, 1215, 1170, 1145, 1095, 1050, 1035, 955, 915, 850, 780, 725, 700, 660 cm^{-1}. Exact mass mol wt. Calcd for $C_{13}H_{15}O_2NSe$: 297.0266. Found: 297.0249. Anal. Calcd for $C_{13}H_{15}O_2NSe$: C, 52.71; H, 5.10; N, 4.73. Found: C, 52.77; H, 5.30; N, 4.60.

4-Methylenecyclohexene. A solution composed of 500 mg (1.69 mmol) of 1-[((2-nitrophenyl)seleno)methyl]-3-cyclohexene in 20 mL of tetrahydrofuran was added to a solution of 505 mg (2.36 mmol) of sodium periodate in 20 mL of a methanol/water (7:3) mixture and stirred at room temperature for 24 h. Pentane and saturated aqueous sodium bicarbonate solution were added. The pentane layer was washed with brine, dried (anhydrous sodium sulfate/potassium carbonate), filtered, and concentrated. The residue was subjected to preparative GLC (10% SE-30, 80 °C), and 50 mg of 4-methylenecyclohexene was isolated. The ^{1}H NMR spectrum of 4-methylenecyclohexene was identical with that reported by Babad et al.:[50] ^{1}H NMR ($CDCl_3$/TMS) δ 5.67 (d, 2 H, olefinic CH, J = 1.5 Hz), 4.73 (br s, 2 H, vinyl CH_2), 2.76 (m, 2 H, doubly allylic CH_2), 2.24 (m, 4 H, allylic CH_2's).

***cis*-Bicyclo[4.1.0]heptane (40).** The method utilized in the synthesis of *cis*-bicyclo[4.1.0]hept-3-ene was also used for the synthesis of **40** according to a modification of the procedure by Paquette.[14]

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Registry No. 9, 84194-54-7; **10**, 119146-73-5; **11**, 101934-24-1; **13**, 25126-93-6; **14**, 53389-31-4; **15**, 84194-49-0; **16**, 119146-74-6; **17**, 84194-50-3; **18**, 84194-51-4; **19**, 84194-52-5; **20**, 84194-53-6; **21**, 71655-17-9; **22**, 59533-63-0; **23**, 101934-25-2; **24**, 101934-26-3; **25**, 119239-81-5; **26**, 101934-27-4; **27**, 119146-75-7; **28**, 119239-82-6; **29**, 16554-83-9; **30**, 119146-76-8; **31**, 119146-77-9; **32**, 36168-41-9; **33**, 6802-78-4; **34**, 119146-78-0; **35**, 119239-83-7; **36**, 70095-44-2; **37**, 70095-43-1; **38** (isomer 1), 119146-72-4; **38** (isomer 2), 119146-79-1; **39**, 110-83-8; **40**, 286-08-8; **43**, 26325-89-3; **44**, 100-40-3; **45**, 4054-38-0; CH_2I_2, 75-11-6; Na_2S, 1313-82-2; $[Rh(CO)_2Cl]_2$, 14523-22-9; $[Rh(CO-D)Cl]_2$, 12092-47-6; 1-cyanonaphthalene, 86-53-3; triflic acid, 1493-13-6; *p*-toluenesulfonic acid, 104-15-4; 1-methylcyclohexa-1,4-diene, 4313-57-9; toluene, 108-88-3; methyl cyclohexenecarboxylate, 6493-77-2; 1-[((2-nitrophenyl)seleno)methyl]-3-cyclohexene, 88090-53-3; 1-(hydroxymethyl)-3-cyclohexene, 1679-51-2; *o*-nitrophenyl selenocyanate, 51694-22-5; 4-methylenecyclohexene, 13407-18-6; 1-ethyl-1,4-cyclohexadiene, 19841-74-8; 4-ethylene-1-cyclohexene, 16631-66-6; 4-isopropylene-1-cyclohexene, 119182-77-3.

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Photodimerization of Isophorone in Supercritical Trifluoromethane and Carbon Dioxide

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Abstract: An examination of the regio- and stereoselectivity for the photodimerization of isophorone in both supercritical CHF_3 and CO_2 as a function of pressure is presented. This selectivity is discussed in terms of solvent polarity and differential solvent reorganization. The stereoselectivity is influenced mostly by solvent reorganization, and the regioselectivity is influenced by both solvent polarity and solvent reorganization. Differential solvent reorganization is shown to exert the dominant effect on the selectivity, and the viability of a supercritical medium as a mechanistic probe is thereby demonstrated.

In their regions of high compressibility, supercritical fluids[3,4] are powerful tools for probing solvent effects in a wide variety of chemical systems.[5-13] Normally, solvent effects in chemical reactions are probed via a change in solvent or a large change in temperature, both of which amount to major perturbations on the particular system studied. The beauty of a supercritical fluid is that a minor perturbation, i.e., a small change in pressure in the vicinity of the critical point, affords a large change in the density-dependent bulk solvent properties such as dielectric constant and viscosity.

Supercritical fluids are well-known for their applications in separations technology.[3] Despite their obvious potential utility, supercritical fluids have only recently been used as media for the study of ground-state chemical reactions.[5-13] Moreover, photochemical and photophysical phenomena in such media are largely unexplored. Squires[14] briefly examined the photochemical cis-trans isomerization of stilbene in CO_2. Leffler[15] studied the photochemical cis to trans relaxation of 4-(diethylamino)-4'-nitroazobenzene in CO_2. In the photophysical realm, Mataga[16] and Kajimoto[17] examined exciplex fluorescence and charge-transfer-state formation, respectively, in CHF_3.

As part of an effort to understand both the behavior of supercritical fluids on a molecular level and the fundamental nature

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