125.07, 113.01, 112.51, 111.08, 80.50, 79.67, 74.43, 67.32, 57.20, 56.04, 55.67, 42.55, 20.71, 15.39; $[\alpha]^{25}_D = -12°$ (c 0.9, CH_2Cl_2).

Acknowledgment. This work has been financially supported by the National Institutes of Health (CA47249). We are grateful to Mr. Scott Miller and Professor David Evans (Harvard University) for providing spectral data and the optical rotation value for compound i and to Ms. Heather L. Nimmons and Mr. Michael Creech for performing mass spectral measurements.

Registry No. **1a**, 134333-46-3; **1b**, 134333-48-5; **1c**, 134451-71-1; **1d**, 134451-72-2; **2a**, 74327-86-9; **2b**, 1125-88-8; **2c**, 59276-32-3; **2d**, 134333-50-9; **2f**, 2186-92-7; **3a**, 134333-47-4; **3b**, 134451-73-3; *anti*-**3c**, 134451-76-6; *syn*-**3c**, 134333-53-2; *anti*-**3d**, 134451-77-7; *syn*-**3d**, 134333-54-3; **3e**, 134333-55-4; **3f**, 134333-56-5; **3g**, 134451-74-4; **3h**, 134333-57-6; **3i**, 134451-75-5; *anti*-**3j**, 134451-78-8; *syn*-**3j**, 134333-58-7; **4a**, 134333-49-6; **4b**, 134333-51-0; **5**, 134333-59-8; $Ph(CH_3)_2SiCH{=}CHCH(CH_3)OCOCH_2OCH_3$, 129921-50-2; $Ph(CH_3)_2SiCH{=}CHCH(CH_3)OCOCH_2CH_3$ (isomer 1), 134333-60-1; $Ph(CH_3)_2SiCH{=}CHCH(CH_3)OCOCH_2CH_3$ (isomer 2), 133323-28-1; $Ph(CH_3)_2SiCH{=}CHCH(CH_3)OC(DTMS){=}CHOCH_3$, 134333-61-2; $Ph(CH_3)_2SiCH{=}CHCH(CH_3)OC(OTBS){=}CHCH_3$, 134333-62-3; $Ph(CH_3)_2SiCH{=}CHCH(CH_3)OC(OTMS){=}CHCH_3$, 134333-63-4; (*R*)-*O*-acetylmandelic acid, 59276-32-3; 3-[(2*S*,3*R*)-3-(2,5-dimethoxy-2-nitrophenyl)-3-methoxy-2-methyl-1-propanoyl]-4-methyl-5-phenyl-2-oxazolidone, 134333-52-1.

Supplementary Material Available: Spectra (IR, ^1H NMR, and ^{13}C NMR) for compounds **1a-d** (^1H NMR only), **3a-j**, and **5** (40 pages). Ordering information is given on any current masthead page.

Anionotropic Rearrangements of *tert*-Butyl- and Adamantylthiiranium Ions into Thietanium Ions. A Novel Case of Selectivity

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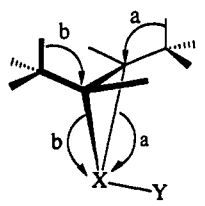
Received February 4, 1991

Abstract: *c*-2-R-*t*-3-R′-*r*-1-Methylthiiranium hexachloroantimonate **6** (R = R′ = *tert*-butyl) converts selectively in CD_2Cl_2 with first-order kinetics to 1,2,2,3-tetramethyl-4-R-thietanium hexachloroantimonate **8** (R = *tert*-butyl), with 4-*tert*-butyl and 3-methyl respectively trans and cis oriented to 1-methyl. The stereospecificity of the rearrangement points to concerted C-S bond breaking and methide migration, with direct generation of the tertiary carbenium ion **20**. The rearrangement was also investigated on isotopomers **9** (**6**, R = *tert*-butyl, R′ = *tert*-butyl-d_9) and **10** (**6**, R = *tert*-butyl-d_9, R′ = *tert*-butyl), and on isomers **15** (**6**, R = *tert*-butyl, R′ = adamantyl) and **16** (**6**, R = adamantyl, R′ = *tert*-butyl). The full kinetic and isotopic analyses for the rearrangements of **9** and **10** show that the methide migration occurs by about 95% from the cis group. Thiiranium **15** converts quantitatively with first-order kinetics to thietanium ion **17** (**8**, R = adamantyl). The rearrangement of the isomer **16** to 3-*tert*-butylhomoadamantylthietanium ion **18** (with the stereochemistry of **8**) is slower and reversible; also the thiiranium ion **15** is formed in the reverse rearrangement, with final irreversible conversion to **17**. The full kinetic analysis of the rearrangement pattern of ion **16** shows that some direct conversion to **17** occurs; the comparison with the rate constant for the rearrangement of **15** suggests that methide migrates preferentially by about 97% from cis *tert*-butyl. The adamantylthiiranium-homoadamantylthietanium equilibrium has also been studied on the diadamantyl derivative **13** (**6**, R = R′ = adamantyl). The selectivity and reversibility in the rearrangements of ions **13** and **16** are consistent with the intermediacy of the nonclassical homoadamantyl carbenium ion **24**; the tertiary endocyclic homoadamantyl carbenium ion **23** may be present along the reaction path, while the secondary exocyclic adamantyl carbenium ion **22** is not involved in the process. Some tentative rationales for this new case of selectivity are proposed.

Introduction

The stereochemical course of concerted [1,2] anionotropic rearrangements is dictated by the requirement of maximum interaction between the orbitals associated with the migrating group and the leaving group (LG); this is reached in the syn- or antiperiplanar reciprocal orientations.[1] In this contest, the preference for antiperiplanarity has been variously attributed to steric effects[2] or to stereoelectronic effects.[1,3] On the other hand, further subtler stereochemical constraints may be induced by an asymmetric LG. We have, in fact, observed a novel type of selectivity in a case where two identical migrating groups are in the same relationship with respect to the bond to be broken, but are differentiated by the X-Y LG, which is not symmetrically oriented:



We have encountered this situation while investigating stable thiiranium and thiirenium ions, the intermediates for the addition of sulfenyl halides to alkenes and alkynes.[4] Our interest was also attracted by the reported[5] stability differences of the adducts of 4-chlorobenzenesulfenyl chloride to (*Z*)- and (*E*)-di-*tert*-butylethylenes **1** and **2a**. While the threo adduct (corresponding to

† Università di Venezia.
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(1) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: Oxford, 1983; Chapter 5.
(2) (a) Sinnott, M. L. *Prog. Phys. Org. Chem.* **1988**, *24*, 113. (b) Selected examples: Sanderson, W. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1966**, *88*, 4185. Guthrie, R. D. *J. Am. Chem. Soc.* **1967**, *89*, 6718. Mosher, H. S. *Tetrahedron* **1974**, *30*, 1733. Domagala, J. M.; Bach, R. D. *J. Am. Chem. Soc.* **1979**, *101*, 3118.
(3) Selected examples: Bates, R. B.; Büchi, G.; Matsuura, T.; Shaffer, R. R. *J. Am. Chem. Soc.* **1960**, *82*, 2327. Yamada, Y.; Kimura, M.; Nagaoka, H.; Ohnishi, K. *Tetrahedron Lett.* **1977**, 2379. Heathcock, C. H.; DelMar, E. G.; Graham, S. L. *J. Am. Chem. Soc.* **1982**, *104*, 1907. Ando, M.; Akahane, A.; Yamaoka, H.; Takase, K. *J. Org. Chem.* **1982**, *47*, 3909.
(4) Capozzi, G.; Lucchini, V.; Modena, G. *Rev. Chem. Intermed.* **1979**, *4*, 347. Capozzi, G.; Modena, G. *Studies in Organic Chemistry 19. Organic Sulfur Chemistry. Theoretical and Experimental Advances*. Bernardi, F., Csizmadia, I. G., Mangini, A., Eds.; Elsevier: New York, 1985; Chapter 5. Capozzi, G.; Modena, G.; Pasquato, L. *The Chemistry of Sulfenic Acids and Their Derivatives*; Patai, S., Ed.; J. Wiley: New York, 1990; Chapter 10.
(5) Dean, C. L.; Garratt, D. G.; Tidwell, T. T.; Schmid, G. H. *J. Am. Chem. Soc.* **1974**, *96*, 4958.

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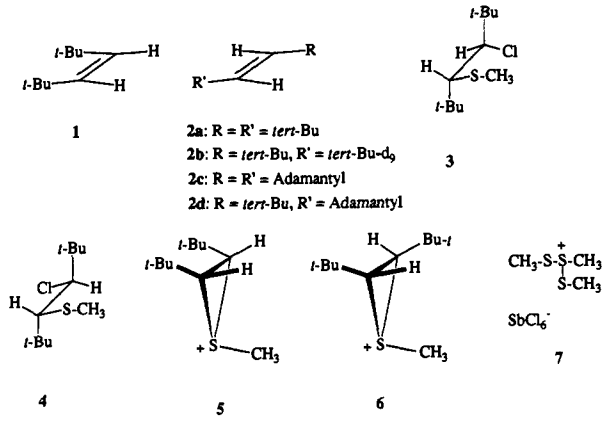
3) is indefinitively stable, the erythro adduct (corresponding to 4) readily gives a rearranged product. Also, the chlorination of the episulfides of **1** and **2a** occurs differently; the former reaction leads to the same compound that is formed by the addition of SCl_2 to **1**, whereas no identified products are obtained from the latter reaction.[6] Moreover, the methylation of the episulfide of **1** gives the stable and isolable thiiranium ion **5**, while the corresponding reaction of the episulfide of **2a** results in noncharacterized products.[6]



In order to determine the origin of these different behaviors, we have undertaken a thorough stereochemical and kinetic investigation of the rearrangement processes of methanesulfenyl chloride adducts of *tert*-butyl and adamantyl 1,2-disubstituted ethylenes and of the corresponding thiiranium ions. A preliminary report has appeared in this journal.[7]

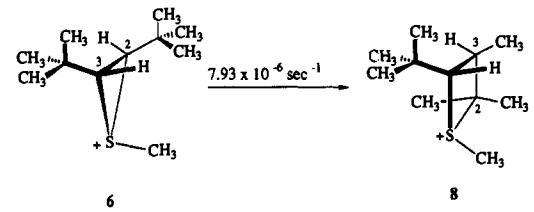
Results

Stability and Rearrangements of *threo*- and *erythro*-3-Chloro-4-(methylthio)-2,2,5,5-tetramethylhexanes (3 and 4). The addition of methanesulfenyl chloride to (*Z*)- and (*E*)-di-*tert*-butylethylenes (**1** and **2a**) parallels that of 4-chlorobenzenesulfenyl chloride.[5] The addition of **1** occurs very rapidly in CH_2Cl_2 as well as in other solvents, and the threo adduct **3** is indefinitely stable both in solution and in the solid state. On the contrary, the addition to **2a** in CH_2Cl_2 is rather slow (about 1 h at room temperature) and the erythro adduct **4** decomposes to a set of products, which were not further investigated. However, if the solvent is swiftly removed and the residue immediately dissolved in liquid SO_2, the ^1H NMR spectrum of *trans,cis*-di-*tert*-butyl-*S*-methylthiiranium (**6**) chloride is immediately observed. The strong ionizing power of liquid SO_2 is well-known and we have already reported processes of this kind for similar substrates.[8] The salt **6** is not stable; it undergoes the unimolecular conversion described below. By contrast, the adduct **3** does not ionize in SO_2.

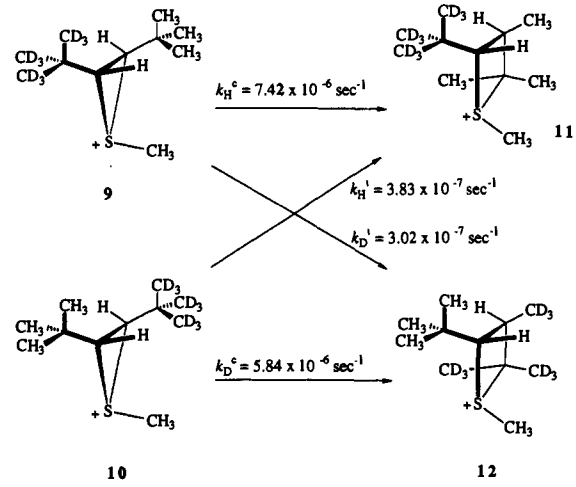
Rearrangements of *trans,trans*- and *cis,trans*-Di-*tert*-butyl-*S*-methylthiiranium Hexachloroantimonates (5 and 6). The isomers **5** and **6** can be easily generated in CH_2Cl_2 or SO_2 by addition of methylbis(methylthio)sulfonium hexachloroantimonate (**7**)[9] to (*Z*)- and (*E*)-di-*tert*-butylethylenes (**1** and **2a**, respectively).[10]

The addition to **1** can, in principle, give rise to two isomeric thiiranium ions, with the *S*-methyl group cis or trans to the *tert*-butyl groups. The trans,trans structure of thiiranium **5** was demonstrated by nuclear Overhauser effect (NOE) analysis,[11] showing relevant dipolar interactions between *S*-methyl and ring

Scheme I



Scheme II



hydrogens (see the Experimental Section). In CD_2Cl_2 at 25 °C this salt slowly converts to several products, among which the chloro adduct **3** was identified by GC–MS. The overall process is likely to be a multistep reaction and was not further investigated.

In trans,cis thiiranium **6**, the resonances of the ring hydrogen and of the *tert*-butyl cis to *S*-methyl have been unambiguously assigned with the aid of NOE analysis. The assignment of the *tert*-butyl resonances is essential for the correct interpretation of the kinetic experiments performed on hemideuterated thiiranium ions **9** and **10** (see below). The ^{13}C resonances of ring carbons at δ 69.60 and 74.82 have been assigned to C2 and C3, respectively, via a heteronuclear shift correlation (H–C COSY) experiment.[12a]

Thiiranium **6** hexachloroantimonate converts quantitatively in about 7 days into thietanium **8** hexachloroantimonate[13] (Scheme I), with a first-order rate constant of 7.93×10^{-6} s^{-1} in CD_2Cl_2 at 25 °C. The ring substituent orientation is inferred from the observation of NOE interactions of the 4-hydrogen with the *S*-methyl and 3-methyl groups. The most deshielded ^{13}C resonances at δ 44.50 (d), 66.08 (s), and 74.36 (d) are attributed to ring C3, C2, and C4, respectively, in agreement with the multiplicities determined with a DEPT experiment.[12b]

Rearrangements of *cis*-*tert*-Butyl-*trans*-*tert*-butyl-d_9-thiiranium Hexachloroantimonate (9) and of *trans*-*tert*-Butyl-*cis*-*tert*-butyl-d_9 Isotopomer 10. The two isotopomeric ions **9** and **10** are obtained in equimolar ratio from the addition of sulfonium salt **7** to (*E*)-*tert*-butyl-*tert*-butyl-d_9-ethylene (**2b**). They give identical resonance patterns, except for the *tert*-butyl resonances at δ 1.36 and 1.18, assigned (from comparison with the resonances of **6**) to **9** and **10**, respectively. The two ions convert to the thietanium ions **11** and **12** (Scheme II), which can be easily distinguished on the basis of the resonance patterns. The first-order rate constants for the disappearance of the *tert*-butyl signals of **9** and **10** are 7.69×10^{-6} and 6.26×10^{-6} s^{-1}, respectively. If the methyl migrations had occurred with the same ease from either the cis or the trans *tert*-butyl group, then the conversion rates of **9** or

(6) Raynolds, P.; Zonnebelt, S.; Bakker, S.; Kellogg, R. M. *J. Am. Chem. Soc.* **1974**, *96*, 3146.
(7) Lucchini, V.; Modena, G.; Pasquato, L. *J. Am. Chem. Soc.* **1988**, *110*, 6900.
(8) Lucchini, V.; Modena, G.; Zaupa, T.; Capozzi, G. *J. Org. Chem.* **1982**, *47*, 590.
(9) Capozzi, G.; Lucchini, V.; Modena, G.; Rivetti, F. *J. Chem. Soc., Perkin Trans. 2* **1975**, 900. Weiss, R.; Schlierf, C. *Synthesis* **1976**, 323.
(10) Capozzi, G.; De Lucchi, O.; Lucchini, V.; Modena, G. *Tetrahedron Lett.* **1975**, 2603.
(11) Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH Publishers: New York, 1989.
(12) (a) Otting, G.; Wüthrich, K. *J. Magn. Reson.* **1988**, *76*, 569. (b) Bendall, M. R.; Doddrell, D. M.; Pegg, D. T.; Hull, W. E. *DEPT*; Bruker special publication: Rheinstetten, FRG.
(13) For other observations of thietanium ions: Trost, B. M.; Schinski, W. L.; Mantz, I. B. *J. Am. Chem. Soc.* **1969**, *91*, 4320. Trost, B. M.; Schinski, W. L.; Chen, F.; Mantz, I. B. *J. Am. Chem. Soc.* **1971**, *93*, 676.

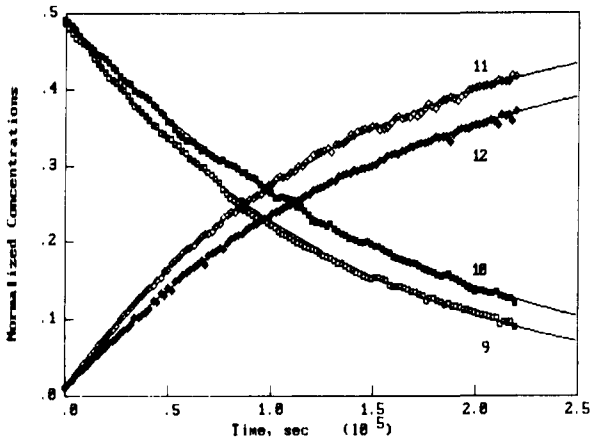


Figure 1. Rearrangements of *tert*-butyl-*tert*-butyl-d_9-thiiranium ions **9** and **10** to thietanium ions **11** and **12** (Scheme II). The corresponding equations given in the Appendix have been fitted to the normalized integrals of the monitored resonances (*tert*-butyl for **9**, **10**, and **12**, and cumulated methyls for **11**) by means of the Simplex procedure.

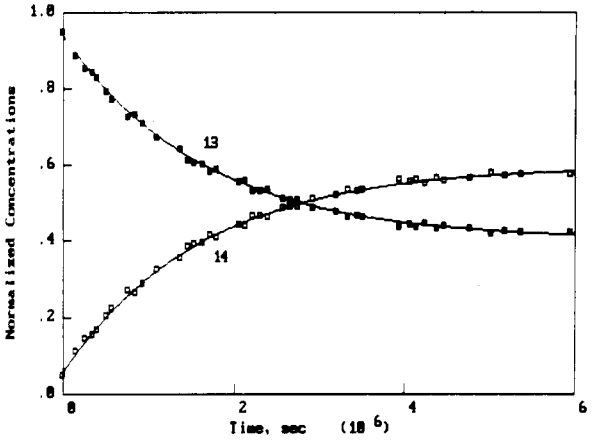
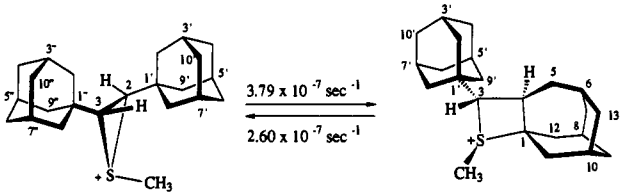


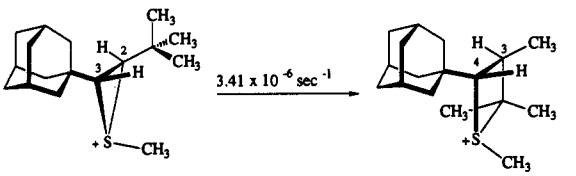
Figure 2. Equilibrium rearrangement of diadamantylthiiranium ion **13** and adamantylhomoadamantylthietanium ion **14** (Scheme III). The equations describing a two-member equilibrium have been fitted to the normalized integrals of the *S*-methyl resonances by means of the Simplex procedure.

Scheme III



13 14

Scheme IV



15 17

10 would have been the same. Actually the conversion of **9** is slightly slower than that of unlabeled thiiranium ion **7** while that of **10** is considerably slower, suggesting that the methide migration preferentially occurs from cis *tert*-butyl. This hypothesis is further substantiated by the fact (cf. Figure 1) that to a faster disappearance of **9** there corresponds a faster appearance of **11**, and that the slower conversion of **10** is paralleled by the slower appearance of the *tert*-butyl resonance of **12**.

If this postulated preference were absolute, then the conversion rates of unlabeled **6** and of **9** should be equal. In order to test whether the detected difference is significant or attributable to experimental errors, the rates of appearance of **11** and **12** must be calculated. As both products may derive from two different reagents at different reaction rates, the Guggenheim treatment cannot be applied.[14] We had therefore to resort to the full integration (by the method of Laplace transforms[15]) of the differential equations describing the kinetic system of Scheme II (the apexes c and t signify rearrangement from the cis and trans groups, respectively), followed by Simplex minimization[16] of the sum of squared differences between calculated and experimental concentrations (see the Experimental Section and the Appendix). As detailed in the Appendix, the Simplex procedure converges univocally when the number of variables (rate constants) is reduced by making the reasonable assumption that the kinetic isotope effect (KIE) is the same for cis and trans rearrangements. The results of Simplex optimization are reported in Scheme II and graphically shown in Figure 1. The optimized KIE is 1.27. The comparison of k^c and k^t shows that the preference degree for cis rearrangement is 95%.

Equilibrium Rearrangement of *cis,trans*-Diadamantyl-*S*-methylthiiranium Hexachloroantimonate (13). The thiiranium ion **13** (Scheme III) is easily prepared from the addition of sulfonium salt **7** to (*E*)-diadamantylethylene (**2c**). The compound has been fully characterized by the ^1H and ^{13}C spectral patterns. The thiiranium ring hydrogen resonances have been assigned with an NOE experiment carried out at −50 °C.[17] The ^{13}C spectrum displays 11 signals that have been assigned (DEPT) to 1 primary, 4 secondary, 4 tertiary, and 2 quaternary carbons. The resonances of the ring carbons next to the sulfonium sulfur occur at δ 68.29 and 74.30, and have been assigned to C2 and C3, respectively (H–C COSY).

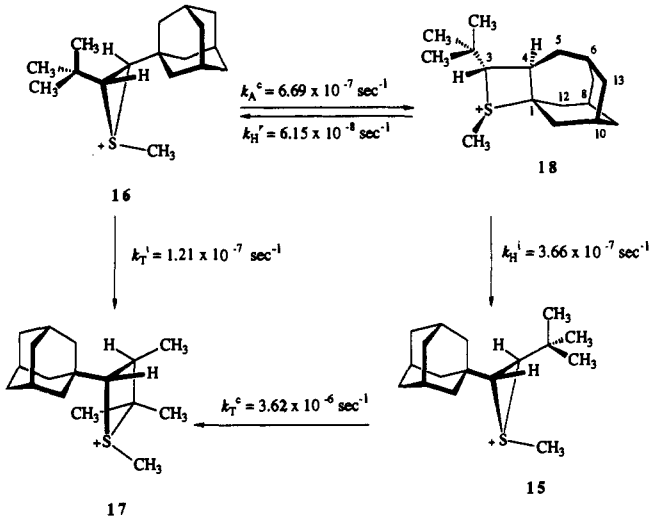
In CD_2Cl_2 the ion slowly reaches an equilibrium with a second species, characterized by the presence of 17 ^{13}C signals assigned (DEPT) to 1 primary, 8 secondary, 6 tertiary, and 2 quaternary carbons. The most deshielded resonances at δ 48.37 (d), 70.09 (s), and 76.49 (d) closely match those of thietanium ion **8**. These findings fully agree with the structure of thietanium ion **14**, possessing one adamantyl and one homoadamantyl skeleton. A dipolar interaction between *S*-methyl and 3-hydrogen was measured in an NOE experiment run at −50 °C.[17] Since the resonances of 5-methylene in the homoadamantyl skeleton and of the 2′-, 8′-, and 9′-methylenes in the adamantyl moiety could not be exactly assigned, the observed interactions with the 2-hydrogen resonance are ambiguous. However, the resonance frequency of the 2-hydrogen is very close to the corresponding resonance in thietanium ion **18** (see below), and the stereochemistry of this latter was then assumed.

The kinetic run was monitored at 25 °C over a period of about 12 weeks (Figure 2). The normalized integrals of the methyl resonances of **13** and **14** have been fitted by the Simplex optimization procedure to the integrated equations describing a two-member equilibrium.[18] The optimized forward and reverse rate constants are reported in Scheme III. Their ratio gives a [thietanium]/[thiranium] equilibrium constant at 25 °C of 1.46.

Rearrangements of *trans*-Adamantyl-*cis*-*tert*-butylthiiranium Hexachloroantimonate (15) and of the *cis*-Adamantyl-*trans*-

(14) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*; Wiley-Interscience: New York, 1981; pp 71 and 287.
(15) Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*; Prentice Hall: Englewood Cliffs, New Jersey, 1989; p 48.
(16) Nash, J. C. *Compact Numerical Methods for Computers*; Adam Hilger Ltd.: Bristol, U.K., 1979; p 141.
(17) In the sample with which we conducted the kinetic run, we could detect no NOE dipolar interactions at 25 °C associated with the *S*-methyl and the ring hydrogen resonances, which are also unusually large. These anomalies disappear at −50 °C.
(18) Reference 15, p 50.

Scheme V



***tert*-butyl Isomer 16.** The two isomers **15** and **16** are readily obtained in CH_2Cl_2 in an almost equimolar ratio from the addition of the sulfonium salt **7** to (*E*)-adamantyl-*tert*-butylethylene (**2d**). The orientation of the *S*-methyl groups have been determined with NOE experiments. The *cis*-*tert*-butylthiiranium salt **15** can be isolated in the form of pure crystals, while the trans isomer **16** is contaminated by 4–5% of **15** (see the Experimental Section). The isomer **15** converts quantitatively to thietanium ion **17** with a first-order rate constant of 3.41×10^{-6} s^{-1} in CD_2Cl_2 at 25 °C (Scheme IV).

As detailed in Scheme V, the rearrangement of the other isomer **16** is more complex. The full kinetic sequence was followed at 25 °C over a period of about 16 weeks by monitoring the *S*-methyl resonances of the species involved. At the beginning, conversion to the homoadamantylthietanium ion **18** is observed. This adamantyl–homoadamantyl rearrangement is also reversible: both thiiranium ions **15** and **16** are generated in the reverse reaction, as is shown by the transient buildup of the former (see Figure 3). Then follows the final and irreversible formation of thietanium ion **17**. It was possible to perform an NOE analysis of the transient species **18** during the kinetic run. Reciprocal enhancements have been detected between the ring 3-hydrogen resonance and those of *S*-methyl and of one homoadamantyl proton (necessarily a 5-methylene proton), thus giving the ring-substituent orientation of structure **18**.

In the kinetic system of Scheme V, the indexes A, T, and H refer to the rearrangements from the adamantyl, *tert*-butyl, and homoadamantyl skeletons. The apexes c and t signify rearrangement from the cis and trans moieties, respectively, while the apexes r and i denote reversion of **18** to the *cis*- and *trans*-adamantylthiiranium ions **16** and **15** (with a retained or inverted configuration at the sulfur). The kinetic run with hemideuterated thiiranium ions **9** and **10** shows that rearrangements from both cis and trans *tert*-butyl groups are possible; thus in the reaction Scheme V, besides k_T^c, k_T^t was also considered. On the other hand, the conversion of pure **15** occurs with rigorous first-order kinetics to only one detectable product; we therefore considered the k_A^t term negligible.

The Laplace transforms of this kinetic system are the integrated expressions for **15**, **16**, **17**, and **18**, which are detailed in the Appendix. Their Simplex fitting into the normalized integrals of the respective *S*-methyl resonances gives the results reported in Scheme V and graphically shown in Figure 3. Inspection of Figure 3 reveals the absence of substantial systematic errors. As revealed by Figures 4 and 5 in the supplementary material, systematic and uneliminable deviations of the computed curves from the experimental points are evident when the rearrangement of **16** is considered to occur exclusively from the cis adamantyl group (k_T^t set to 0), or when the back-conversion of **18** is considered to give **15** and **16** with equal ease (k_H^i mantained equal to k_H^r).

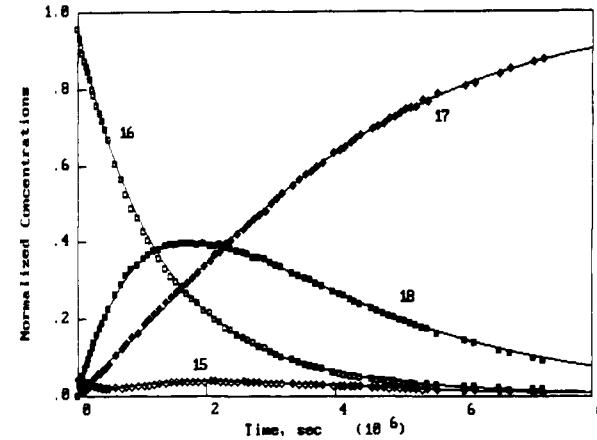


Figure 3. Rearrangements of adamantyl-*tert*-butylthiiranium ions **15** and **16** and thietanium ions **17** and **18** (Scheme V). The corresponding equations given in the Appendix have been fitted to the normalized integrals of the *S*-methyl resonances by means of the Simplex procedure. All rate constants have been optimized.

As expected, k_T^c is equal, within experimental and computational errors, to the conversion rate constant of pure **15**. Moreover, comparison of k_T^c and k_T^t reveals that the methide migration occurs with a preference degree of 97% from the cis rather than from the trans *tert*-butyl group.

Discussion

While the adduct **3** is indefinitely stable, the isomer **4** readily rearranges and decomposes in solvents such as $CDCl_3$ or CD_2Cl_2. In liquid SO_2 **3** is again stable, but **4** solvolyzes instantaneously to *cis,trans*-di-*tert*-butylthiiranium (**6**) chloride, which then slowly rearranges to thietanium **8** chloride. The different behaviors of **3** and **4** in this efficiently ionizing solvent[8] may be explained by the fact that the heterolysis of chloride ion requires the participation of the sulfide sulfur in antiperiplanar orientation. Both the inspection of molecular models and MM2 molecular mechanics computations[19] show that the conformational preferences of **3** and **4** are determined by the nonbonding repulsion of the *tert*-butyl groups, which are fixed in an anti orientation. Therefore in **3**, the sulfide sulfur is oriented gauche with respect to chlorine and cannot provide any assistance to ionization.

On the other hand, the presence of a thiiranium ion intermediate is not, as such, a sufficient condition for the occurrence of a rearrangement process; the *trans,trans*-di-*tert*-butylthiiranium ion **5**, related to the adduct **3**, does not undergo the rearrangement observed for the cis,trans ion **6**.

Concertedness of C–S Bond Breaking and Methide (or Methylenide) Migration. Two nonconcerted mechanistic alternatives may be proposed: (i) fast equilibrium between a thiiranium ion of type **6** and a secondary carbenium ion **19** (Scheme VI), followed by rate-determining methide migration, or (ii) rate-determining formation of **19** followed by fast methide migration, but neither is consistent with the results described below. The possibility of fast equilibrium is ruled out by the lack of direct conversion between stereoisomeric ions **15** and **16**, which may only occur via the intermediacy of thietanium ion **18**.[20]

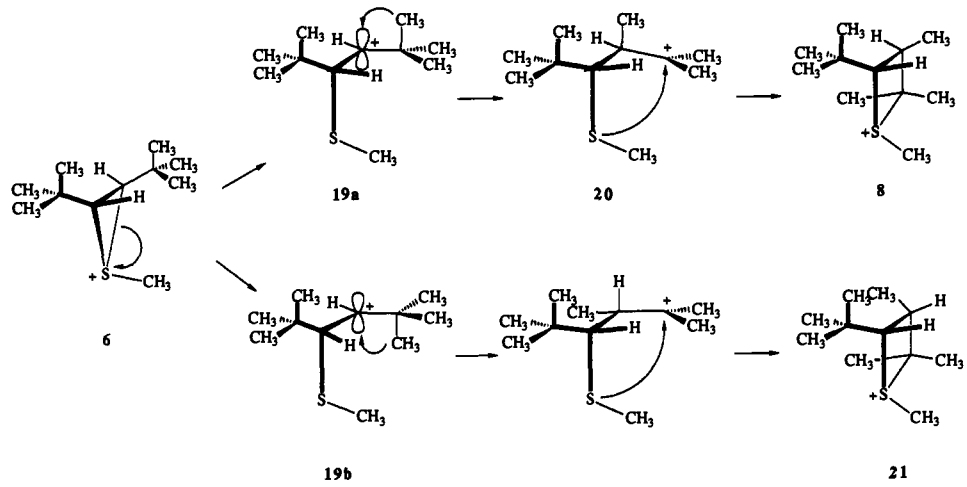
The intermediacy of **19** is also inconsistent with the specific formation of only one isomeric thietanium ion. The requirement of maximal orbital overlap[21] is satisfied in both conformers **19a** and **19b**, which would lead to stereoisomeric thietanium ions **8** and **21**, respectively. No significant energy difference may be associated with **19a** and **19b**, although the former may be thought

(19) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

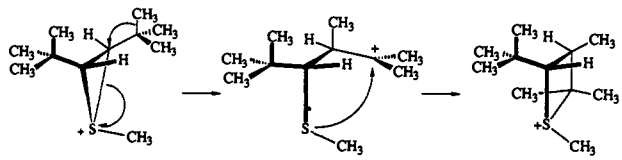
(20) Also, no direct interconversion of **5** and **6** could be observed. This fact may, however, find alternative explanations.

(21) Brouwer, D. M.; Hogeveen, H. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 211. Schleyer, P. v. R.; Lam, L. K. M.; Raber, D. J.; Fry, J. L.; McKervey, M. A.; Alford, J. R.; Cuddy, B. D.; Keizer, V. G.; Geluk, H. W.; Schlatmann, J. L. M. A. *J. Am. Chem. Soc.* **1970**, *92*, 5246. Majerski, Z.; Schleyer, P. v. R.; Wolf, A. P. *J. Am. Chem. Soc.* **1970**, *92*, 5731.

Scheme VI



Scheme VII



to originate directly from the preferred conformation of **6** with staggered orientation of the cis *tert*-butyl group. Therefore, the specific formation of **8** requires that the lifetime of **19** be shorter than the rotational time of the *tert*-butyl group. This assumption becomes inconsistent when the reversible adamantyl–homoadamantyl rearrangements of thiiranium ions **13** and **16** are considered. The principle of microscopic reversibility will require the presence of the same intermediate (with structure **22**, see below) in the forward and reverse rearrangements. Contradictorily, the lifetime of this intermediate should be shorter than the rotational time of the adamantyl group, but longer than the vibrational time necessary for bringing the sulfur atom close to the carbenium carbon.

Also, the KIE of 1.27 measured for the conversions of hemideuterated ions **9** and **10** cannot be explained by a nonconcerted mechanism. This value may be adequate as an α KIE in the case of alternative (i), already excluded. If alternative (ii) holds, then this is a γ KIE. Substantial remote KIEs are indicative of strong relief of the nonbonding interaction from a congested initial structure to a less congested transition state.[22] Although the conversion of **6** (or of the isotopomers **9** or **10**) to an intermediate of type **19** involves some steric relief, oure measured KIE is noticeably greater than that reported for a more congested substrate.[23]

Under the hypothesis of a concerted mechanism (Scheme VII), the C–S bond breaking is assisted by migration of a methide group from one *tert*-butyl moiety, with direct formation of the tertiary carbenium ion **20**. Then the sulfur atom closure to the electron-deficient carbon will yield only one thietanium ion, with exactly the ring substituent orientation found in **8**.

Within this mechanistic hypothesis, the KIE is an α effect. The value of 1.27 is, however, much greater than that reported[24] for a methide migration from a perdeuterated *tert*-butyl group. The small isotope effect found in this instance arises from the compensation of the normal effect of the migrating group and the reverse effect of the nonmigrating ones.[25] A relatively small isotope effect has been associated with a transition state with poor C_α–C_γ interaction.[24] Thus the greater effect found in our rearrangement may well be indicative of a stronger (and indeed decisive) participation of methide migration in the C–S bond breaking. We cannot, of course, rule out that the steric relief on going from **6** (or from **9** or **10**) to **20** (or corresponding structures) may contribute to some degree to the measured KIE.

The Methide (or Methylenide) Group Migrates Preferentially from the Group Cis to *S*-Methyl. The observation that the rearrangement occurs in thiiranium ion **6** but not in isomer **5** may suggest that the methide migrates preferentially or exclusively from the *tert*-butyl group cis to the *S*-methyl.

This selectivity is confirmed by the consideration of the first-order rate constants measured for the disappearance of hemideuterated thiiranium ions **9** and **10**. The mere existence of an isotope effect is a clear indication that the methide migrations from cis and trans *tert*-butyl groups occur under different controlling features. If we assume the exclusive cis migration, then the KIE is normal (1.23) and in accordance with the postulated mechanism. The hypothesis of exclusive trans migration gives a reverse KIE value of 0.81, which is clearly untenable. The full kinetic analysis (Scheme II) gives a preference for the cis rearrangement of 95% and a correct KIE of 1.27.

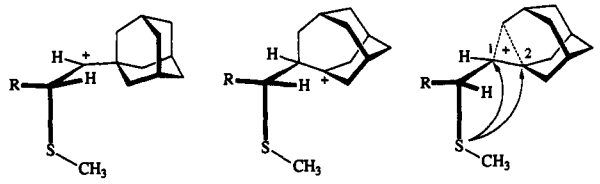
The cis selectivity is further confirmed by the observation that the faster disappearance of **9** is associated with the faster formation of thietanium ion **11** (with migration of CH_3), while the conversion of **10** and the formation of **12** (with migration of CD_3) are slower.

Definitive evidence for the selectivity of the methide migration is offered by the rearrangement processes of the two isomeric adamantyl-*tert*-butylthiiranium ions **15** and **16**. Thiiranium ion **15**, with a cis *tert*-butyl group, undergoes quantitative first-order conversion to thietanium ion **17**. On the other hand, it is mainly the cis adamantyl residue of thiiranium ion **16** that rearranges to give **18** at a rate about 5 times slower than that observed in the conversion of **15**, but still about 5 times faster than the methide migration from the trans *tert*-butyl group. When this latter rate constant (k_T^t in Scheme V) is compared with that for the migration from the cis *tert*-butyl group (from conversion of **15**, or k_T^c in Scheme V), the cis selectivity amounts to 97%. This degree is to be compared with that (95%) found for the rearrangements of hemideuterated thiiranium ions **9** and **10**.

Structure of the Intermediate Cation and Stereochemical Consequences. At variance with the case of thiiranium ions, the C–S bond breaking in thietanium ions **14** and **18** may occur unassisted, as it leads directly to the tertiary carbenium ion **23**. On the other hand, the closure of the sulfur atom to give thiiranium ions **13**, **15**, or **16** requires either the intermediacy of the secondary carbenium ion **22** (already excluded from the reaction path) or attack on **23** by nucleophilic sulfur at the carbon next to the positive center, with displacement of the methylenide group. This requires a significant delocalization of the positive charge on this carbon, so that the intermediate may be better described as the nonclassical

(22) Carter, R. E.; Melander, L. *Adv. Phys. Org. Chem.* **1973**, *10*, 1.
(23) Fry, J. L.; Badger, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 6276.
(24) Ando, T.; Yamataka, H.; Morisaki, H.; Yamawaki, J.; Kuramochi, J.; Yukawa, Y. *J. Am. Chem. Soc.* **1981**, *103*, 430.
(25) Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. In *Ions and Ion Pairs in Organic Reactions*; Szwark, M., Ed.; Wiley: New York, 1974; Vol. 2, p 247.

homoadamantyl cation **24**.[26] This latter may stand alone along the reaction path or may be in equilibrium with **23**.[27]



22 **23** **24**

R = *tert*-Bu, Adamantyl

Indeed, the nonclassical ion **24** may cleanly rationalize the observed 5:1 selectivity in the formation of thiiranium ions **15** and **16** from thietanium ion **18**. As in other nonclassical ions,[28] the sp^2-hybridized C1 and C2 centers interact with the bridging carbon with one lobe of the p orbital, leaving the other free for a nucleophilic attack.[29] The formation of **15** or **16** requires that the *pro-R* or *pro-S* sulfur lone pair (defined with reference to the enantiomers shown in structures **22–24**) points along the free lobe at C1, with nonbonding interactions of *S*-methyl with the *tert*-butyl group or the homoadamantyl skeleton, respectively; the two groups have comparable bulkiness, but the former is free to rotate, and can better accommodate the methyl.

On the other hand, the selective *S*-methyl orientation in thietanium ions **14** and **18** may be explained by the intermediacy of **24** as well as by that of **23**. In the same manner, the *S*-methyl orientation in thietanium ions **8** and **17** may be accounted for by an intermediate with structure **20**. This orientation requires the nucleophilic attack of the *pro-S* sulfur lone pair along the direction of the free lobe at C2 in **24** or the vacant p orbital in **23**, while the *pro-R* lone pair points toward the unrearranged *tert*-butyl or adamantyl group and the methyl is in the middle free region. In the case of attack by the *pro-R* lone pair, there results nonbonding interaction between the methyl group and the unrearranged group.

The homoadamantyl skeleton is estimated to be 8–11 kcal mol^{-1} more strained than the adamantyl skeleton.[30] The equilibrium constant for the reaction in Scheme III says that homoadamantylthietanium ion **14** is about 0.2 kcal mol^{-1} more stable than adamantylthiiranium ion **13**,[31] while the relief of nonbonding interaction between *S*-methyl and *tert*-butyl or adamantyl on going from **7** to **8** or from **15** to **17** may account for 1.8–2.0 kcal mol^{-1} at most.[32] Thus we may consider the thietanium ring less strained by 6–9 kcal mol^{-1} than the thiiranium ring. The irreversibility in the *tert*-butyl rearrangement of **6** or **15** is to be ascribed to this ring stabilization.

Conclusions

At the present stage, our investigation offers a satisfactory answer about the modality of the rearrangement process, but can only give tentative suggestions concerning the reasons for the strong selectivity observed. It may be argued that the nonbonding interaction between the cis *tert*-butyl or adamantyl group and *S*-methyl in thiiranium ions may exert a greater steric strain on the underlying C–S bond. A weaker bond also implies a greater positive charge at the carbon terminus and a greater contribution of sp^2 hybridization, with the possibility of a greater interaction of a more developed vacant p orbital with the migrating bond. However, it should be noticed that the ^{13}C chemical shifts of ring carbons in thiiranium ions **6** and **13** do not conform to this description.

Alternatively, under the hypothesis of stereoelectronic control, it may be suggested that orbitals localized at the sulfur–methyl bond combine with orbitals at ring carbons with correct symmetry. One such combination may be a low-lying vacant orbital with a deeper expansion in the hemispace containing the sulfur–methyl bond, and is therefore able to interact more efficiently with a migrating bond in the cis group.

Also, the reasons for the different behavior of trans,trans and trans,cis thiiranium ions **5** and **6** are presently not understood. We can only suggest that the ring carbons in **5** may be less shielded from the attack of an external nucleophile than those in **6**.

In order to answer these questions, we are undertaking ab initio computations on model molecules of **5** and **6**, and are also subjecting the hexachloroantimonates of **5** and **6** to diffractometric analysis.

Experimental Section

General. Melting points, measured with a Büchi 510 apparatus, are uncorrected. ^1H and ^{13}C NMR spectra, kinetic measurements, NOE determinations,[11] DEPT experiments,[12b] and heterocorrelated H–C COSY experiments[12a] were performed on Bruker AC200 and AM400 spectrometers. Photochemical reactions were carried out in a Rayonet photochemical reactor equipped with a 254-nm source. GC–MS analyses were performed with a 5890–5940 Hewlett-Packard instrument. Commercial reagents were purified to match the reported physical and spectral data. Solvents were dried according to standard procedures.

Nuclear Overhauser Effect Determinations.[11] The samples (in CD_2Cl_2) were freed from O_2 by sonication under N_2 purging. The usual procedure for gated irradiation experiments was modified,[33] and the selected resonance was saturated by a 10-s cyclic perturbation of all lines with a 40–45 dB attenuation of a nominal 0.2-W decoupling power. A reference spectrum was acquired by setting the decoupler frequency off-resonance. The enhancements were obtained from the multiplier of the reference spectrum which brings the observed multiplet to exactly match the corresponding multiplet in the perturbed spectrum. Errors are estimated to be ca. 0.3%. Only those results relevant for structural determinations are reported, with the following convention. Observed nucleus H_a: {saturated nucleus H_b}, percent enhancement and or comments, repeat for other saturated nuclei.

Kinetic Measurements. The first-order conversions of thiiranium ions **6** and **15**, the equilibrium rearrangements of **13** and **14**, and the complex interconversions of **16**, **14**, **15**, and **17** were followed by measuring the integrated area of the *S*-methyl resonances. The rearrangements of hemideuterated thiiranium ions **9** and **10** to thietanium ions **11** and **12** were followed by monitoring the intensities of the *tert*-butyl resonances of **9**, **10**, and **12** and the cumulated intensities of ring 2- and 3-methyl resonances of **11**. The complex kinetic runs of Schemes II, III, and V had to be followed almost to completion over a period of 1–16 weeks; in order to compensate for the changing spectrometer conditions, the monitored intensities were normalized against their sum. These values were fitted to the equations given in the Appendix or in ref 18 by means of the Simplex procedure.[16] The optimized rate constants are estimated to be correct to 2 significant figures.

(*Z*)- and (*E*)-Di-*tert*-butylethylene (1 and 2a). These olefins were prepared by literature procedure.[34] In every synthetic step the solvent was removed by distillation at atmospheric pressure. The isomers were separated by preparative GC (house-made instrument) on a SE-30 column at 50 °C. **1**, ^1H NMR (200 MHz, $CDCl_3$): δ 1.15 (s, *t*-Bu), 5.20

(26) The nature of the intermediate in adamantyl–homoadamantyl rearrangements is controversial: Nordlander, J. E.; Jindal, S. P.; Schleyer, P. v. R.; Fort, R. C., Jr.; Harper, J. J.; Nicholas, R. D. *J. Am. Chem. Soc.* **1966**, *88*, 4475. Liggero, S. H.; Sustmann, R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1969**, *91*, 4571. Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1973**, *95*, 194. Bentley, T. W.; Liggero, S. H.; Imhoff, M. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 1970. Olah, G. A.; Prakash, G. K. S.; Liang, G.; Schleyer, P. v. R.; Graham, W. D. *J. Org. Chem.* **1982**, *47*, 1040. Wilgis, F. P.; Neumann, T. E.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4435.

(27) However, it must be pointed out that ab initio calculations of the most investigated pair of classical-nonclassical systems (the 2-norbornyl cation) have found only one minimum on the potential surface: Yoshimine, M.; McLean, A. D.; Liu, B. *J. Am. Chem. Soc.* **1983**, *105*, 6185.

(28) Winstein, S.; Shatavsky, M. *J. Am. Chem. Soc.* **1956**, *78*, 592. Winstein, S.; Hansen, R. L. *Tetrahedron Lett.* **1960**, No. *25*, 4. Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 6803.

(29) The ab initio fully optimized geometry of nonclassical 2-norbornyl cation at a high computational level gives C1 and C2 atoms with a trigonal-pyramidal bond arrangement: Goddard, J. D.; Osamura, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1982**, *104*, 3258.

(30) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891. Müller, P.; Blanc, J.; Mareda, J. *Helv. Chim. Acta* **1986**, *69*, 635.

(31) $\Delta G° = 1.4 \log K$ at 25 °C.

(32) This estimate is calculated[31] from the k^c/k^t ratios, under the hypothesis that the cis selectivity is induced exclusively by this nonbonding interaction (see the Conclusions Section).

(33) Kinns, M.; Sanders, J. K. M. *J. Magn. Reson.* **1984**, *56*, 518.

(34) Puterbaugh, W. H.; Newmann, M. S. *J. Am. Chem. Soc.* **1959**, *81*, 1611.

(s, olefinic H). **2a**, ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.97 (s, *t*-Bu), 5.32 (s, olefinic H).

(*E*)-*tert*-Butyl-d_9-*tert*-butylethylene (2b). The hemideuterated olefin was prepared with the procedure described above by using deuterated acetone and deuterated bromomethane.[35] The mixture of cis and trans isomers was irradiated in methanol until the cis isomer was no longer detected by GC–MS.

(*E*)-Diadamantylethylene (2c),[36] This olefin was obtained from the corresponding alkyne[37] by PtO_2-catalyzed hydrogenation. The *E* isomer is directly obtained. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.5–2.0 (multiplets, 30 H, adamantyl), 5.11 (s, olefinic H).

Adamantyl-*tert*-butylethyne.[38] Freshly sublimed aluminum trichloride (87 mg, 0.1 equiv) is added in one step at −60 °C to a solution of *tert*-butyl(trimethylsilyl)acetylene[39] (1.0 g) and adamantyl bromide (1.4 g) in 50 mL of dry CH_2Cl_2. After 20 min the reaction is poured in ca. 50 mL of water, and the organic layer is washed with saturated $NaHCO_3$ and dried over $MgSO_4$. The solvent is rotoevaporated and the product purified by chromatography (substrate–silica gel ratio 1:10, eluant light petroleum), yielding 1.3 g (93%) of colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.17 (s, *t*-Bu), 1.6–1.9 (multiplets, 15 H, adamantyl).

(*E*)-Adamantyl-*tert*-butylethylene (2d). PtO_2 (80 mg, 0.05 equiv) is added to a solution of 1 g of adamantyl-*tert*-butylethyne in 50 mL of ethanol. The reaction vessel is attached to a three-way stopcock, fitted with a H_2-filled balloon and a water pump. The pressure is reduced until the solvent starts boiling and then H_2 is let in. The procedure is repeated three times. Under the H_2 pressure provided by the balloon, the reaction is complete in 40 min (as monitored by GC–MS). The mixture is filtered through a layer of silica gel, and the layer washed with CH_2Cl_2. The concentrated filtrate gives 1.01 g of crude **2d** (100%). The product was purified by distillation, bp 80–81 °C at 0.3 mmHg. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.97 (s, *t*-Bu), 1.5–2.2 (multiplets, adamantyl), 5.15 and 5.27 (doublets, olefinic H, J = 16.2).

(3*R,4*R**)-3-Chloro-4-(methylthio)-2,2,5,5-tetramethylhexane (3),**[6] ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.12 and 1.17 (singlets, *t*-Bu), 2.20 (s, 4-CH_3), 2.81 and 4.08 (doublets, olefinic H, J = 3.7).

(3*S,4*R**)-3-Chloro-4-(methylthio)-2,2,5,5-tetramethylhexane (4).** This compound has been generated and observed in an NMR tube by addition of freshly prepared methanesulfenyl chloride to **2a** in CD_2Cl_2. Any attempted isolation led to decomposition. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.06 and 1.08 (singlets, *t*-Bu), 2.15 (s, 4-CH_3), 2.51 and 4.09 (doublets, olefinic H, J = 0.6).

General Procedure for the Synthesis of Thiiranium Ions.[10] Methylbis(methylthio)sulfonium hexachloroantimonate (**7**)[9] (0.6 mmol) is added in one step to a solution of 0.7 mmol of the olefin in 10 mL of dry CH_2Cl_2. After 10 min of magnetic stirring, pentane is added and the precipitate filtered off. The salts can be further purified by crystallization from CH_2Cl_2 at low temperature. The isotopomers **9** and **10** are obtained in a 1:1 ratio. The stereoisomers **15** and **16** are also obtained in a 1:1 ratio. The thiiranium salt **15** with cis *tert*-butyl precipitates in the form of pure crystals from the mixture of the two isomers in CH_2Cl_2 at −18 °C. From the mother liquor a solid consisting of salt **16** with trans *tert*-butyl, contaminated by 4–5% of **15**, is recovered.

***t*-2,*t*-3-Di-*tert*-butyl-*r*-1-methylthiiranium Hexachloroantimonate (5),** ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.35 (s, *t*-Bu), 2.88 (s, 1-CH_3), 4.33 (s, H2 and H3). ^{1}H NOE (200 MHz, CD_2Cl_2) *t*-Bu: {H2 and H3}, 1.2; 1-CH_3: {*t*-Bu}, 1.0, {H2 and H3}, 2.2; H2 and H3: {*t*-Bu}, 6.5, {1-CH_3}, 2.5. Anal. Calcd for $C_{11}H_{23}Cl_6SSb$: C, 25.32; H, 4.44. Found: C, 24.84; H, 4.42.

***c*-2,*t*-3-Di-*tert*-butyl-*r*-1-methylthiiranium Hexachloroantimonate (6),** ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.18 (s, 3-*t*-Bu), 1.36 (s, 2-*t*-Bu), 2.88 (s, 1-CH_3), 3.74 (d, H2, $J_{2,3}$ = 13.7), 4.09 (d, H3). ^{1}H NOE (200 MHz, CD_2Cl_2) 3-*t*-Bu: {H2}, 0.9, {H3}, 0.9; 2-*t*-Bu: {1-CH_3}, 1.2, {H2}, 0.9, {H3}, 0.9; 1-CH_3: {2-*t*-Bu}, 1.7, {H3}, 1.1; H2: {3-*t*-Bu}, 6.8, {2-*t*-Bu}, 6.1; H3: {3-*t*-Bu}, 4.5, {2-*t*-Bu}, 3.7, {1-CH_3}, 1.8. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 18.84 (q, 1-CH_3), 27.18 (q, 3-C(CH_3)$_3$), 29.08 (q, 2-C(CH_3)$_3$, 33.43 and 35.00 (singlets, 2- and 3-C(CH_3)$_3$), 69.60 (d, C2), 74.82 (d, C3). Anal. Calcd for $C_{11}H_{23}Cl_6SSb$: C, 25.32; H, 4.44. Found: C, 24.87; H, 4.30.

***c*-2,*t*-3-Diadamantyl-*r*-1-methylthiiranium Hexachloroantimonate (13),** ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.5–2.2 (multiplets, 30 H, adamantyl skeletons), 2.90 (s, 1-CH_3), 3.58 (d, H2, $J_{2,3}$ = 12.5), 3.96 (d, H3). ^{1}H NOE (400 MHz, CD_2Cl_2, −50 °C) 1-CH_3: {H3}, 1.8; H3: {1-CH_3}, 4.2. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 20.10 (q, 1-CH_3), 27.93 and 28.28 (doublets, C3′, C5′, and C7′ or C3″, C5″, and C7″), 35.862 and 35.868 (triplets, C4′, C6′, and C10′ or C4″, C6″, and C10″), 34.56 and 36.92 (singlets, C1′ or C1″), 40.22 and 41.62 (triplets, C2′, C8′, and C9′ or C2″, C8″, and C9″), 68.29 (d, C2), 74.30 (d, C3). Anal. Calcd for $C_{23}H_{35}Cl_6SSb$: C, 40.74; H, 5.20. Found: C, 39.15; H, 4.47.

***t*-3-Adamantyl-*c*-2-*tert*-butyl-*r*-1-methylthiiranium Hexachloroantimonate (15),** ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.34 (s, *t*-Bu), 1.5–2.2 (multiplets, 15 H, adamantyl), 2.83 (s, 1-CH_3), 3.78 (d, H2, $J_{2,3}$ = 13.4), 3.96 (d, H3). ^{1}H NOE (400 MHz, CD_2Cl_2) *t*-Bu: {1-CH_3}, 0.8, {H2}, 1.1, {H3}, 0.9; 1-CH_3: {*t*-Bu}, 3.3, {H3}, 1.4; H2: {*t*-Bu}, 10.9; H3: {*t*-Bu}, 6.2, {1-CH_3}, 2.5.

***c*-2-Adamantyl-*t*-3-*tert*-butyl-*r*-1-methylthiiranium Hexachloroantimonate (16),** ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.16 (s, *t*-Bu), 1.5–2.2 (multiplets, 15 H, adamantyl), 2.93 (s, 1-CH_3), 3.53 (d, H2, $J_{2,3}$ = 13.4), 4.08 (d, H3). ^{1}H NOE (400 MHz, CD_2Cl_2) *t*-Bu: {H2}, 0.8, {H3}, 0.9; 1-CH_3: {H3}, 1.2; H2: {*t*-Bu}, 11.9; H3: {*t*-Bu}, 8.4, {1-CH_3}, 2.5. Anal. (for the mixture of **15** and **16**) Calcd for $C_{17}H_{29}Cl_6SSb$: C, 34.03; H, 4.87. Found: C, 33.96; H, 4.97.

Thietanium Ions. Thietanium ions **8** and **17** are stable and can be isolated and characterized by elemental analysis. The nonseparable hemideuterated thietanium ions **11** and **12** (showing some resonances isotopically shifted with respect to those of **8**) and the thietanium ions **14** and **18**, transient or in equilibrium, have been characterized spectroscopically.

***t*-4-*tert*-Butyl-*r*-1,2,2,*c*-3-tetramethylthietanium Hexachloroantimonate (8),** ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.12 (s, *t*-Bu), 1.26 (d, 3-CH_3, J_{HCCH} = 6.8), 1.777 and 1.781 (singlets, 2-(CH_3)$_2$), 3.06 (s, 1-CH_3), 3.12 (dq, H3), 3.74 (d, H4, $J_{3,4}$ = 11.4). ^{1}H NOE (200 MHz, CD_2Cl_2) *t*-Bu: {H3}, 1.0, {H4}, 0.6; 3-CH_3: {H3}, 2.2, {H4}, 0.8; 1-CH_3: {H4}, 0.7; H3: {*t*-Bu}, 8.5, {3-CH_3}, 6.9; H4: {*t*-Bu}, 3.7, {3-CH_3}, 1.8, {1-CH_3}, 3.3. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 16.36 (q, 3-CH_3), 19.08 and 29.36 (quartets, 2-(CH_3)$_2$), 23.87 (q, 1-CH_3), 26.84 (q, C(CH_3)$_3$), 33.96 (s, C(CH_3)$_3$), 44.50 (d, C3), 66.08 (s, C2), 74.36 (d, C4). Anal. Calcd for $C_{11}H_{23}Cl_6SSb$: C, 25.32; H, 4.44. Found: C, 24.74; H, 4.33.

***t*-4-*tert*-Butyl-d_9-*r*-1,2,2,*c*-3-tetramethylthietanium Hexachloroantimonate (11),** ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.26 (d, 3-CH_3, J_{HCCH} = 6.8), 1.780 and 1.785 (singlets, 2-(CH_3)$_2$), 3.06 (s, 1-CH_3), 3.12 (dq, H3), 3.75 or 3.76 (d, H4, $J_{3,4}$ = 11.4).

***t*-4-*tert*-Butyl-*r*-1-methyl-2,2,*c*-3-trimethyl-d_3-thietanium Hexachloroantimonate (12),** ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.12 (s, *t*-Bu), 3.06 (s, 1-CH_3), 3.11 (br d, H3), 3.75 or 3.76 (d, H4, $J_{3,4}$ = 11.4).

(2*S,3*S**,4*R**)-2-Methyl-3-adamantyltetracyclo[6.3.1.$1^{1,8}$.$1^{6,10}$.$0^{1,4}$]tridecane-2-thionium Hexachloroantimonate (14),** ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.5–2.5 (multiplets, 30 H, adamantyl and homoadamantyl skeletons), 2.95 (s, 1-CH_3), 3.30 (m, H4), 3.72 (d, H3, $J_{3,4}$ = 12.6). ^{1}H NOE (400 MHz, CD_2Cl_2, −50 °C) 1-CH_3: {H3}, 0.8; H3: {1-CH_3}, 3.3; H4: {H5 or H2′, H8′, and H9′}, 3.6. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 22.86 (q, 1-CH_3), 27.93 (d, C3′, C5′, and C7′), 28.91 (d), 29.73 (d), 31.12 (d), 33.87 (t), 35.09 (t), 35.30 (s, C1′), 36.08 (t, C4′, C6′, and C10′), 37.06 (t), 39.98 (t, C2′, C8′, and C9′), 40.65 (t), 42.76 (t), 47.95 (t), 48.37 (d, C4), 70.09 (s, C1), 76.49 (d, C3).

***t*-4-Adamantyl-*r*-1,2,2,*c*-3-tetramethylthietanium Hexachloroantimonate (17),** ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.25 (d, 3-CH_3, J_{HCCH} = 6.9), 1.5–2.1 (multiplets, 15 H, adamantyl), 1.76 (s, 2-(CH_3)$_2$), 3.03, (s, 1-CH_3), 3.18 (dq, H3, $J_{3,4}$ = 11.4), 3.58 (d, H4). ^{1}H NOE (400 MHz, CD_2Cl_2) 3-CH_3: {H3}, 0.7, {H4}, 1.9; 1-CH_3: {H4}, 0.9; H3: {3-CH_3}, 6.5; H4: {3-CH_3}, 3.1, {1-CH_3}, 3.4. Anal. Calcd for $C_{17}H_{29}Cl_6SSb$: C, 34.03; H, 4.87. Found: C, 33.92; H, 4.58.

(2*S,3*S**,4*R**)-2-Methyl-3-*tert*-butyltetracyclo[6.3.1.$1^{1,8}$.$1^{6,10}$.$0^{1,4}$]tridecane-2-thionium Hexachloroantimonate (18),** ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.10 (s, *t*-Bu), 1.5–2.5 (multiplets, 15 H, homoadamantyl skeleton), 2.98 (s, 1-CH_3), 3.23 (m, H4), 3.88 (d, H3, $J_{3,4}$ = 12.5). ^{1}H NOE (400 MHz, CD_2Cl_2) *t*-Bu: {H3} and {H4}, not detected; 1-CH_3: {H3}, 0.5; H3: {1-CH_3}, 2.8, {*t*-Bu}, 10.6; H4: {*t*-Bu}, 13.1.

Appendix

The differential equations describing kinetic Scheme II are as follows:

$$d[9]/dt = -(k_H^c + k_D^t)[9]$$

$$d[10]/dt = -(k_D^c + k_H^t)[10]$$

$$d[11]/dt = k_H^c[9] + k_H^t[10]$$

$$d[12]/dt = k_D^c[10] + k_D^t[9]$$

The integrated equations are as follows:

(35) Weiner, N. *Organic Syntheses*; Blatt, A. H., Ed.; J. Wiley: New York, 1943; Collect. Vol. II, p 280.
(36) Adam, W.; Martinez, G.; Thompson, J.; Yany, F. *J. Org. Chem.* **1981**, *46*, 3359.
(37) Capozzi, G.; Romeo, G.; Marcuzzi, F. *J. Chem. Soc., Chem. Commun.* **1982**, 959.
(38) Capozzi, G.; Ottanà, R.; Romeo, G.; Marcuzzi, F. *Gazz. Chim. Ital.* **1985**, *115*, 311.
(39) Zweifel, G.; Lewis, W. *J. Org. Chem.* **1978**, *43*, 2739.

$$[9] = [9]_0e^{-\lambda_1 t}$$

$$[10] = [10]_0e^{-\lambda_2 t}$$

$$[11] = [11]_0 - [9]_0k_H^c(e^{-\lambda_1 t} - 1)/\lambda_1 - [10]_0k_H^t(e^{-\lambda_2 t} - 1)/\lambda_2$$

$$[12] = [12]_0 - [9]_0k_D^t(e^{-\lambda_1 t} - 1)/\lambda_1 - [10]_0k_D^c(e^{-\lambda_2 t} - 1)/\lambda_2$$

where

$$\lambda_1 = k_H^c + k_D^t$$

$$\lambda_2 = k_D^c + k_H^t$$

This system of equations is underdetermined as the Simplex procedure converges to different sets of optimized variables, depending on the input set. The convergence is univocal when the number of variables is reduced by the substitutions $k_H^c = ik_D^c$ and $k_H^t = ik_D^t$, where the KIE i is assumed to be the same for the cis and trans rearrangements.

The differential equations describing kinetic Scheme V are as follows:

$$d[16]/dt = k_H^r[18] - (k_A^c + k_T^t)[16]$$

$$d[18]/dt = k_A^c[16] - (k_H^r + k_H^i)[18]$$

$$d[15]/dt = k_H^i[18] - k_T^c[15]$$

$$d[17]/dt = k_T^c[15] + k_T^t[16]$$

The integrated equations are as follows:

$$[16] = Ae^{-\lambda_1 t} + Be^{-\lambda_2 t}$$

$$[18] = C(e^{-\lambda_1 t} - e^{-\lambda_2 t})$$

$$[15] = De^{-\lambda_1 t} + Ee^{-\lambda_2 t} + (F + [15]_0)e^{-\lambda_3 t}$$

$$[17] = [16]_0b/\lambda_1\lambda_2 + [15]_0 + Ge^{-\lambda_1 t} + He^{-\lambda_2 t} + (I - [15]_0)e^{-\lambda_3 t}$$

where

$$\lambda_1, \lambda_2 = (a \pm \sqrt{(a^2 - 4b)})/2$$

$$\lambda_3 = k_T^c$$

$$a = k_A^c + k_H^r + k_H^i + k_T^t$$

$$b = k_A^ck_H^i + k_T^t k_H^i + k_T^t k_H^r$$

$$A, B = [16]_0(k_H^r + k_H^i - \lambda_{1,2})/(\lambda_{2,1} - \lambda_{1,2})$$

$$C = [16]_0k_A^c/(\lambda_2 - \lambda_1)$$

$$D, E, F = [16]_0k_A^ck_H^i/(\lambda_{2,1,1} - \lambda_{1,2,3})(\lambda_{3,3,2} - \lambda_{1,2,3})$$

$$G, H = [16]_0k_T^t(k_H^r + k_H^i - \lambda_{1,2})/\lambda_{1,2}(\lambda_{2,1} - \lambda_{1,2}) + [16]_0k_A^ck_H^ik_T^c/\lambda_{1,2}(\lambda_{2,1} - \lambda_{1,2})(\lambda_3 - \lambda_{1,2})$$

$$I = [16]_0k_A^ck_H^i/(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)$$

Supplementary Material Available: Figures 4 and 5 graphically illustrating the presence of systematic errors when the rearrangements of ions **15**, **16**, **17**, and **18** are fitted into the equations in the Appendix, constraining k_T^t to 0 or k_H^i and k_H^r to the same value (3 pages). Ordering information is given on any current masthead page.

Cyclizations of Unsaturated $\cdot CR(COX)_2$ Radicals. Manganese(III) Acetate Oxidative Cyclizations of Unsaturated Acetoacetates and Atom-Transfer Cyclizations of Unsaturated Haloacetoacetates Give the Same Radicals

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Abstract: Comparable regio- and stereochemical results were obtained when cyclizations of a series of 2-substituted 3-oxohept-6-enoate (or oct-7-enoate) esters (acetoacetates) were conducted by manganese(III) acetate oxidation or by iodine or bromine atom transfer cyclization. The observed trends support the conclusion that free radicals **6b** (rather than Mn(III)-complexed radicals **5b**) are involved in the Mn(III)-mediated oxidative cyclization of tertiary malonates and acetoacetates. Most cyclizations proceeded under kinetic control, and several showed large temperature dependences on stereoselectivity. An apparent discrepancy was resolved by demonstrating that ring opening of radical **43** (a reverse 6-exo cyclization) was faster than bromine transfer, but slower than iodine transfer or Cu(II) oxidation. In the process of ring closure/ring opening, a *Z*-alkene is converted to an *E*-alkene. Since the *E*- and *Z*-alkenes provide distinct stereochemical results on cyclization, the observed stereochemical ratio becomes a very sensitive probe for this radical ring opening. This observation presages the design and use of related probes for radical ring opening.

Introduction

Radical cyclizations of alkenes have rapidly emerged as powerful reactions for ring construction.[2] The precursors and the products for such cyclizations can vary as a function of the method chosen to conduct the cyclization, and methods based on reduction, isomerization, and oxidation are popular. Oxidative methods have

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