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An Authentic Case of In-Plane Nucleophilic Vinylic Substitution: The Anionotropic Rearrangement of Di-*tert*-butylthiirenium Ions into Thietium Ions[†]

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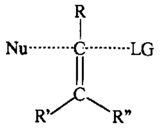
Abstract: *S*-Methyl- and *S*-(4-chlorophenyl)-substituted di-*tert*-butylthiirenium ions **7a** and **7b** rearrange quantitatively with first-order kinetics to thietium ions **8a** and **8b**. The specificity of the rearrangement and the relevant secondary kinetic isotope effect observed with *S*-(4-chlorophenyl)thiirenium ion **7c** perdeuteriated at one *tert*-butyl group point to an intramolecular concerted in-plane vinylic substitution (S_N2-Vin mechanism). The comparison with the rearrangements from *trans-tert*-butyl in *S*-methylthiiranium ions **4a** and **4b** (occurring with intramolecular S_N2 mechanism) gives $k(S_N2)/k(S_N2\text{-Vin})$ ratios ranging from 12 to 720.

The bimolecular nucleophilic substitutions at alkylic sp^3 carbon and at vinylic sp^2 carbon cannot be easily compared. The nucleophilic attack at alkylic carbon occurs along the direction of the leaving group (LG) and from the back side, goes through a transition state with pentacoordinate carbon, and generates inverted products (S_N2 mechanism). The logical vinylic analogue to this mechanism would be the attack of the nucleophile in the molecular plane to give, through the planar transition state **1**, an inverted product (S_N2-Vin mechanism).[1,2]



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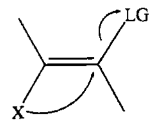
This mechanism however occurs very seldom: in almost every situation the nucleophile approaches the vinylic carbon perpendicularly, goes through a tetrahedral intermediate, and gives a configurational output that ranges from retention to stereoconvergence (Ad$_N$-E mechanism).[2,3] Therefore only the perpendicular attack has been extensively studied from a theoretical perspective,[4] and only one rather old report has appeared assessing the preference for the perpendicular attack over the in-plane one.[5] The in-plane possibility has been dismissed also on the argument of steric hindrance of the approaching nucleophile with the substituents at the vinyl system.[6] Partial or even complete inversion, however, has been found in the nucleophilic displacement of vinyl triflates[7] and of vinyl iodonium salts,[8] *i.e.* in systems possessing a particularly good leaving group. The stereochemical outcome has been rationalized by the intermediacy of an ion pair[7] or has been left unexplained.[8]

There are two special olefinic systems where the in-plane S_N2-Vin attack with complete configurational inversion is strongly preferred or exclusive. These are systems **2** and **3**, where the nucleophile or the LG is directly bonded to the other terminus of the olefinic bond.[9]



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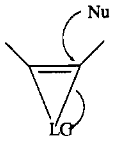

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The two systems differ in one substantial point: in system **2** the nucleophile is geometrically constrained to the in-plane attack and hence to the S_N2-Vin mechanism. Examples for this reaction scheme are given by the solvolyses of vinylic substrates with participation of β-sulfur,[10] β-iodine,[11] or β-aryl.[12] In system **3** both in-plane S_N2-Vin and perpendicular Ad$_N$-E mechanisms are in principle possible and have been in fact documented. Exclusive inverted products are obtained from nucleophilic attack to irenium ions possessing a neutral LG (thiirenium[13,14] and selenirenium[15] ions), while retention of configuration is observed with thiirene 1,1-dioxide, with an anionic LG.[16] The rationalization presented for this different behavior[9a] is not totally satisfactory.

Systems **2** and **3** are logically connected, as the latter may derive from the former; therefore solvolyses occurring with

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[†] Dedicated to Professor D. E. Sunko on the occasion of his 70th birthday.

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(7) Summerville, R. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 1110.

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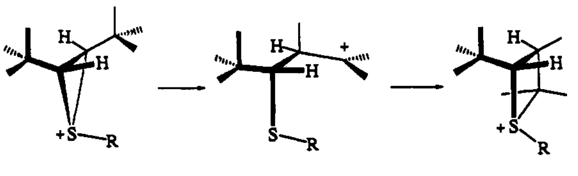
Scheme I



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4a, 5a, 6a: R = CH_3
4b, 5b, 6b: R = 4-Cl-C_6H_4

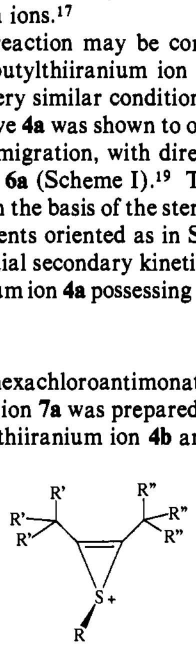
nucleophilic neighboring-group participation may end up with retention of configuration through a double inversion.

We will present in this paper a further example of the rare S_N2-Vin mechanism: the rearrangement of di-*tert*-butylthiirenium ions (*S*-methyl- and *S*-(4-chlorophenyl)-substituted) into thietium ions.[17]

The reaction may be compared with the rearrangement of di-*tert*-butylthiiranium ion **4** into thietanium ion **5**, occurring under very similar conditions. The conversion of the *S*-methyl derivative **4a** was shown to occur via concerted ring opening and methyl migration, with direct generation of the inverted intermediate **6a** (Scheme I).[19] The concertedness was firmly established on the basis of the stereospecific formation of **5a** (with the substituents oriented as in Scheme I) and of the detection of a substantial secondary kinetic isotope effect (KIE) measured on thiirenium ion **4a** possessing one perdeuteriated *tert*-butyl group.

Results

The hexachloroantimonate salt of di-*tert*-butyl-*S*-methylthiirenium ion **7a** was prepared as described.[13] The corresponding salts of thiiranium ion **4b** and thiirenium ion **7b** were prepared



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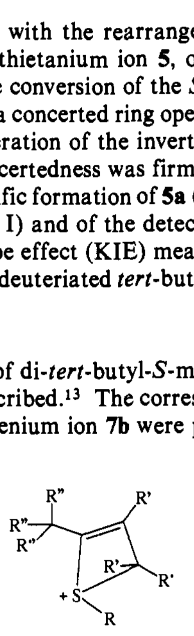

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7a, 8a: R = R' = R" = CH_3
7b, 8b: R = 4-Cl-C_6H_4, R' = R" = CH_3
7c, 8c: R = 4-Cl-C_6H_4, R' = CH_3, R" = CD_3
8d: R = 4-Cl-C_6H_4, R' = CD_3, R" = CH_3

by the reaction of (4-chlorophenyl)bis((4-chlorophenyl)thio)sulfonium hexachloroantimonate[20] with *trans*-di-*tert*-butylethylene and di-*tert*-butylacetylene, respectively. In turn, the sulfonium salt was obtained by the same procedure described for methylbis(methylthio)sulfonium hexachloroantimonate.[21] The salts **7a,b** are stable in the solid form for some days at room temperature. The salt **4b** shows an incipient rearrangement already during the preparative stage and has to be utilized immediately.

Table I. First-Order Rate Constants for the Rearrangements of Thiiranium and Thiirenium Ions **4** and **7**, in CD_2Cl_2 at 25 °C

compound	k^{-1}, s^{-1}	compound	k^{-1}, s^{-1}
4a[a]	7.93×10^{-6} [b]	**7a**	6.30×10^{-8}
	7.42×10^{-6} [c]	**7b**	3.93×10^{-6}
	3.83×10^{-7} [d]	**7c**	1.85×10^{-6} [e]
4b	2.83×10^{-3} [b]		1.55×10^{-6} [f]

[a] Reference 19. [b] "Overall" migration rate. [c] Migration from *cis-tert*-butyl. [d] Migration from *trans-tert*-butyl. [e] k_H: migration of CH_3. [f] k_D: migration of CD_3.

The rearrangements of salts **4b** and **7a,b** into thietanium **5b** and thietium **8a,b** ions,[22] respectively are quantitative. The first-order rate constants in CD_2Cl_2 at 25 °C are collected in the Table I. The rearranged products **5b** and **8a,b** were unambiguously characterized by the NMR resonance pattern and, in some cases, by the net of the NOE interactions[23] (see Experimental Section).

Further information on the mechanism for the rearrangement of thiirenium ions was gained by measuring the KIE of thiirenium ion **7c** perdeuteriated at one *tert*-butyl group. The results are graphically displayed in Figure 1 and reported in Table I. The KIE is 1.19. The k_H value is in good agreement (statistical factor of 2) with the rate constant measured for the light compound **7b**.

Discussion

Concertedness of the Rearrangement. In strict correspondence with the process of the saturated analogue,[19] the concertedness of the rearrangement of thiirenium ions **7** is based upon the following considerations.

(i) The thietium ions **8a,b** are formed quantitatively from ions **7a,b** and the partially deuteriated thietium ions **8c,d** are the sole products arising from the rearrangment of **7c**. This selectivity is consistent with a concerted process, occurring with the intermediacy of the *E* tertiary carbenium ion **9a** (path b in Scheme II). The nonassisted heterolysis of the methylthio LG (path a) would have led to the linear vinyl cation intermediate **10**, which would in principle undergo a methyl shift to either lobe of the vacant vinyl p orbital to generate the *Z*–*E* pair of tertiary carbenium ions **9a** and **9b**. Only the former can close to the thietium ion, while the latter would evolve by reacting with adventitious nucleophiles or bases to give either an addition or an elimination product.

It should be noticed that the substituents at the *β*-carbon may influence the methyl migration, and actually the *tert*-butyl group has been found very effective in directing the nucleophilic attack to the opposite side.[24] Thus the nonconcerted process would preferentially lead to products other than **8**.

In principle **9a** and **9b** may evolve to the corresponding planar allylic cations. If this process actually occurs in **9a**, it must be reversible, as the ring closure to **8** requires the "perpendicular" conformation.

(ii) The secondary KIE is relevant for the rearrangements of both the thiiranium ion[19] and thiirenium ion, and it is more in agreement with a concerted mechanism (where it is an *α* effect) than with a nonconcerted one (a *γ* effect). Remote secondary KIEs have been justified with other rationals, noticeably with the relief of steric strain from a congested initial structure to a less congested transition state.[25] This factor may play some role in the rearrangement of thiiranium ions **4**, but it is certainly less determining in the conversion of thiirenium ions **7**. It is in any case greater than that reported for a more congested substrate.[26]

For the sake of completeness, the alternative Ad_N-E mechanism (Scheme III) should be considered. It would go through the

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(17) This rearrangement has been preliminarily reported in ref 18.

(18) Capozzi, G.; Modena, G.; Pasquato, L. *The Chemistry of Sulfenic Acids and Their Derivatives*; Patai, S., Ed.; J. Wiley: Chichester, U.K. 1990; Chapter 10.

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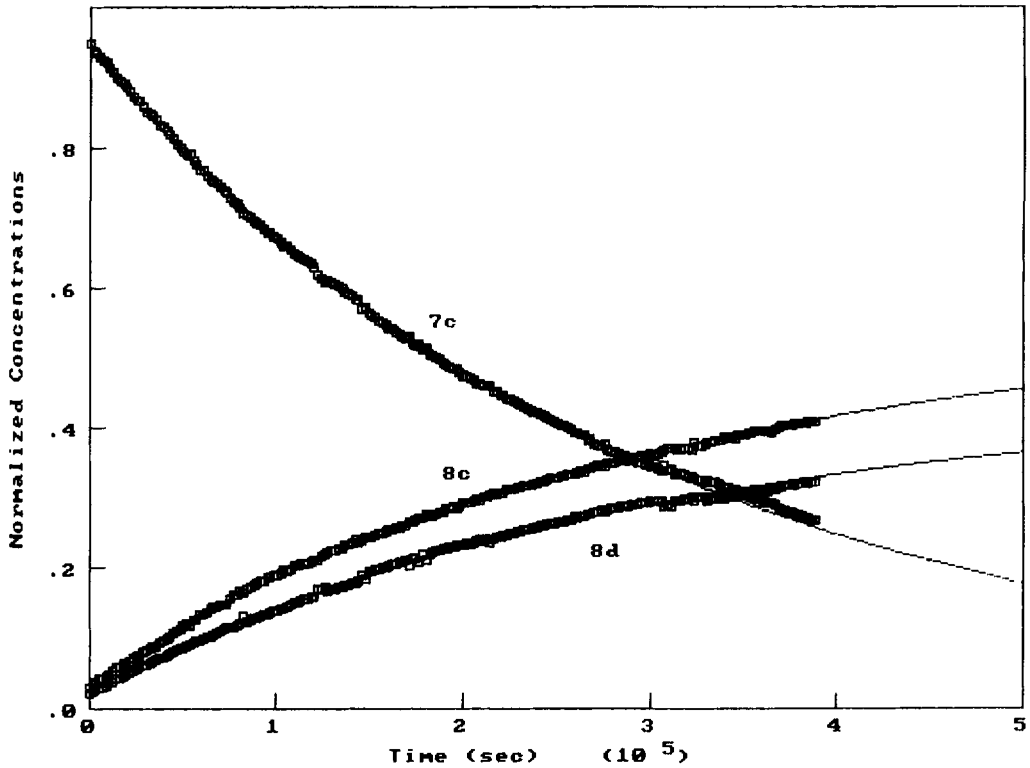
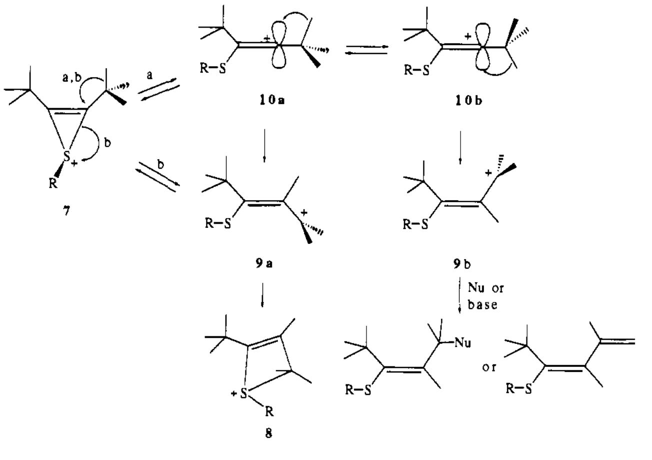
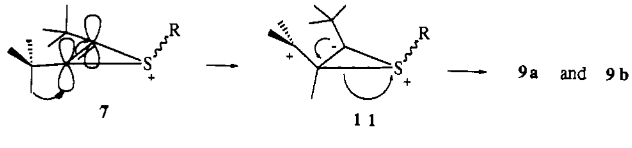


Figure 1. Rearrangement of *tert*-butyl(*tert*-butyl-d$_9$)thiirenium ion **7c** into thietium ions **8c** and **8d**. The equations for unimolecular competitive reactions have been fitted to the normalized integrals of the monitored resonances (*tert*-butyl for **7c** and **8d**, and cumulated methyls for **8c**).

Scheme II



Scheme III



ylide intermediate **11**, which in principle may evolve to both **9a** and **9b**. The mechanism is consistent with the observed α KIE, and even a specific conversion to **9a** cannot be excluded. Ylide **11** however should be considered a high-energy intermediate in a process where the ring strain relief of **7** (one major factor favoring the S_N2-Vin mechanism[9]) is not operative.

Other examples of alkyl rearrangement to the double bond in solvolytic reactions have been reported.[27] In some instances the rearrangement was taken as evidence for the vinyl cation intermediacy;[28] in other cases the anchimeric assistance of the migrating group to the LG heterolysis was suggested but not proved.[29] The evidence we are presenting strongly supports an intramolecular in-plane S_N2-Vin mechanism for the rearrangement of thiirenium ions.

Comparison between the S_N2-Vin and S_N2 Mechanisms. A number of factors may affect the S_N2-Vin mechanism in systems **2** and **3** with respect to the alkylic S_N2 counterpart: (i) The inversion of configuration requires a pyramidal inversion at an sp^3 carbon and an in-plane inversion at an sp^2 carbon, which is energetically more costly.[30] (ii) In both systems **2** and **3**, some hindrance may be exerted by the substituent geminal to the LG, which lies in the same plane of the approaching nucleophile;[6] in the alkylic S_N2 reaction, the geminal substituents are below and above this plane. Factors i and ii will negatively affect the S_N2-Vin mechanism. (iii) The antiaromatic character of the pyramidal thiirenium ion, although strongly reduced with respect to that of a generic planar irene ion,[31] and (iv) the strain of the unsaturated cycle, greater than that of the saturated one,[32] will both disfavor the ring closure reaction of system **2** but will facilitate the ring-opening reaction of system **3**.

A comparison between the solvolyses of aliphatic and vinylic substrates with anchimeric participation of the β-thio group (system **2**) is not easily accomplished. Most information for vinylic substitutions derives from our old investigations on the solvolyses of β-thiovinyl trinitrobenzenesulfonates.[10] The corresponding solvolyses of β-thioalkyl substrates do not necessitate such a strong nucleofuge: toluenesulfonates **12a** and **12b** solvolyze at 25 °C with rate constants of 1.97×10^{-3} and 1.45×10^{-3} s^{-1}, respectively.[33] No data are available for the solvolyses of the corresponding vinyl toluenesulfonates **13a** and **13b**, but values of 1.62×10^{-8} and 1.88×10^{-9} s^{-1} can be estimated (from the solvolysis rates of vinyl trinitrobenzenesulfonates **13c** and **13d**,[10]

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[27] Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinylic Cations*; Academic Press: New York, 1979; p 453.

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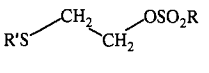
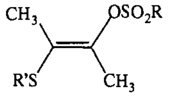
[30] Cf. the energetics for pyramidal inversion of trialkylamines and for in-plane inversion of imines: Koeppl, G. W.; Sagatys, D. S.; Krishnamurthy, G. S.; Miller, S. I. *J. Am. Chem. Soc.* **1967**, *89*, 3396.



12a: R = $4\text{-}CH_3\text{-}C_6H_4$, R' = CH_3
12b: R = $4\text{-}CH_3\text{-}C_6H_4$, R' = C_6H_5

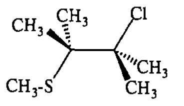


13a: R = $4\text{-}CH_3\text{-}C_6H_4$, R' = CH_3
13b: R = $4\text{-}CH_3\text{-}C_6H_4$, R' = C_6H_5
13c: R = $2,4,6\text{-}NO_2\text{-}C_6H_2$, R' = CH_3
13d: R = $2,4,6\text{-}NO_2\text{-}C_6H_2$, R' = C_6H_5

4.07×10^{-4} and 4.70×10^{-5} s^{-1} at 25 °C, corrected by the vinylic nucleofugality factor[34] of 2.5×10^4). These values give $k(S_N2)/k(S_N2\text{-Vin})$ ratios of 1.2×10^5 and 7.7×10^5 for the rate ratios of solvolyses anchimerically assisted by the methylthio and the phenylthio groups, respectively.

It should be considered that the available nucleofugality scales[34] are based on a series of unassisted solvolytic processes (described by the k_C rate constant). The anchimerically assisted (k_Δ) or nucleophilically solvent assisted (k_S) mechanisms are governed by a less pronounced nucleofugality dependence.[35] Also a comparison based on the degree of anchimeric assistance as measured by the k_Δ/k_S or k_Δ/k_C ratios is not without reservations. In the case of aliphatic substitution, k_Δ and k_S refer to the same mechanism, but most probably two different mechanisms operate in the case of vinylic substitution. Therefore the above estimates of the $k(S_N2)/k(S_N2\text{-Vin})$ ratios are only indicative.

The aliphatic chloride **14** and the vinyl chloride **15** ionize in liquid sulfur dioxide at 25 °C with rate constants of 10.0 and 1.23 $\times 10^{-4}$ s^{-1}, respectively,[36] corresponding to a $k(S_N2)/k(S_N2\text{-Vin})$ ratio of 8.1×10^4. Also this value must be considered cautiously: the LG is the same, but the ionization of the tertiary chloride **14** may be unassisted.



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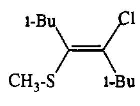

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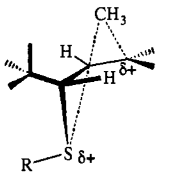
Although these ratios are biased, on the side of vinylic substitution, by the presence of the in-plane geminal substituent and by the formation of the more strained irenium ring, they remain substantial. These relevant ratios may then be related to the fact that in system **2** the geometrically obliged approach does not necessarily correspond to the favored path for nucleophilic substitution.

A second example of the S_N2-Vin mechanism is given by the nucleophilic substitution in thiirenium ions (system **3**), occurring with exclusive formation of inverted trans adducts. A quantitative kinetic investigation is however prevented by the circumstance that in these ions (and in thiiranium ions as well) sulfonium sulfur appears to be significantly more electrophilic than either ring carbon,[18] so that with most reagents partial or total reversion to the hydrocarbon precursors is observed.[37]

This inconvenience is absent in the intramolecular nucleophilic rearrangements of thiiranium ions **4** and thiirenium ions **7**. Also, as illustrated by transition states **16** and **17**, the nucleophilic methyl groups can approach the relevant sp^3 or sp^2 ring carbon virtually unhindered.



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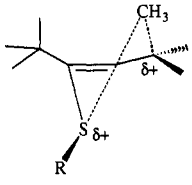

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The $k_{4a}/k_{7a} = 1.3 \times 10^2$ and $k_{4b}/k_{7b} = 7.2 \times 10^2$ ratios give the $k(S_N2)/k(S_N2\text{-Vin})$ ratios for methylthio and (4-chlorophenyl)thio LG, respectively. However in thiirenium **4a** the methyl group migrates predominantly from the *tert*-butyl groups cis to the *S*-methyl group rather than from the trans group.[19] (The same should be true for the rearrangement of ion **4b**, although only one "overall" rate could be determined.) Then, more correctly, two $k(S_N2)/k(S_N2\text{-Vin})$ ratios can be determined, give by $k_{4a}^{\text{cis}}/k_{7a} = 2.4 \times 10^2$ and $k_{4a}^{\text{trans}}/k_{7a} = 12$ (a statistical factor of 2 has been introduced). A preliminary quantum mechanical investigation[37] has linked the preference for cis migration mostly to steric factors: the relief of nonbonding interaction between *cis-tert*-butyl and *S*-methyl on going from ground state **4** to transition state **6**. The comparison of the conversion rate of thiirenium **7a** is therefore more correctly done with the trans conversion rate of **4a** than with the cis rate.

This time the $k(S_N2)/k(S_N2\text{-Vin})$ ratios may be biased in the opposite direction by the greater strain relief of thiiranium ring opening, which may confer to the thio group a better LG ability. Also taking into account this fact, the ratios remain remarkably lower than those found for the substitution in system **2**. It may be suggested that in thiirenium ions the approaching direction of the nucleophile corresponds to the energetically preferred path. The stereoelectronic preference for the S_N2-Vin mechanism may be linked to the presence of a neutral and particularly efficient LG. The precocious propensity to detachment of a very good LG may confer some vinyl cation character to the vinylic substrate, thus favoring the in-plane attack of the nucleophile. The stereochemical course of nucleophilic substitutions in other noncyclic vinyl compounds[7,8] may perhaps be similarly rationalized.

Experimental Section

General Methods. Melting points, measured with a Büchi 510 apparatus, are uncorrected. ^{1}H NMR spectra and NOE determinations were performed on Bruker AC200 and AM400 spectrometers. Commercial reagents and known compounds used in this research were either purchased from standard chemical suppliers or prepared according to literature procedures and purified to match the reported physical and spectral data. Solvents were purified according to standard procedures.

Nuclear Overhauser Effect Determination.[23] The experiments were performed as previously described.[19b] Only those results relevant for structural determinations or resonance assignments are reported, with the following convention. Observed nucleus Ha: {saturated nucleus Hb} percent enhancement and/or comments, repeat for other saturated nuclei.

Kinetic Measurements. The first-order conversions of thiirenium ions **7a** and **7b** were followed by measuring the integrated area of the *tert*-butyl resonance. The rearrangement of hemideuteriated thiirenium ion **7c** to thietium ions **8c** and **8d** was followed by monitoring the intensities of the *tert*-butyl resonances of **7c** and **8d** and the cumulated intensities of the ring 2- and 3-methyl resonances of **8c**. Very slow conversions have been monitored, at appropriate intervals of time, using NMR tubes equipped with air-tight screw caps and kept in a thermostated bath.[19b] In order to compensate for the varying spectrometer conditions, the monitored intensities were normalized against their sum. The integrated

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equations for competitive first-order reactions[38] were fitted to the normalized intensities with the Simplex procedure.[39]

_r_-1-(4-Chlorophenyl)-_c_-2,_t_-3-di-_tert_-butylthiiranium Hexachloroantimonate (4b). (4-Chlorophenyl)bis-((4-chlorophenyl)thio)sulfonium hexachloroantimonate[20] (0.6 mmol) was added in one step to a solution of 0.7 mmol of the olefin in 15 mL of dry CH_2Cl_2 under argon. After 2 min of magnetic stirring, pentane was added and the solution separated from the precipitate. The salt obtained was dried with a vacuum pump and immediately used. ^1H NMR (200 MHz, CD_2Cl_2) δ: 1.07 and 1.32 (singlets, 2-*t*-Bu and 3-*t*-Bu), 4.22 and 4.73 (doublets, H2 and H3, J = 13.7), 7.66 and 7.75 (multiplets, Ar).

_t_-4-_tert_-Butyl-_r_-1-(4-chlorophenyl)-2,2,_c_-3-trimethylthietanium Hexachloroantimonate (5b). ^1H NMR (200 MHz, CD_2Cl_2) δ: 1.16 (s, *t*-Bu), 1.36 (d, 3-CH_3, $J_{HCCH} = 6.9$), 1.41 (s, *c*-2-CH_3), 1.87 (s-*t*-CH_3), 3.26 (dq, H3, $J_{3,4} = 11.3$), 4.42 (d, H4), 7.75 and 7.82 (multiplets, Ar). ^1H NOE (200 MHz, CD_2Cl_2) *t*-Bu: {H3} 0.5, {H4} 0.4. 3-CH_3: {H3} 1.9, {H4} 0.7. *c*-2-CH_3: {*t*-2-CH_3} 0.6, {H4} 0.4, {Ar} 0.5. *t*-2-CH_3: {*c*-2-CH_3} 1.0, {H3} 1.0. H3: {*t*-Bu} 9.9, {3-CH_3} 6.1, {*t*-2-CH_3} 5.9, {H4} 2.2. H4: {*t*-Bu} 4.1, {3-CH_3 and *c*-2-CH_3} 2.5, {H4} 2.5 {Ar} 4.8. Ar: {*c*-2-CH_3} 0.8, {H4} 1.5. Anal. Calcd for $C_{16}H_{24}Cl_7SSb$: C, 31.08, H, 3.91. Found: C, 30.64; H, 3.67.

2,3-Di-_tert_-butyl-1-methylthiirenium Hexachloroantimonate (7a).[10] ^1H NMR (200 MHz, CD_2Cl_2) δ: 1.52 (s, 2-*t*-Bu and 3-*t*-Bu), 2.67 (s, 1-CH_3).

2,3-Di-_tert_-butyl-1-(4-chlorophenyl)thiirenium Hexachloroantimonate (7b). (4-Chlorophenyl)bis-((4-chlorophenyl)thio)sulfonium hexachloroantimonate[20] (0.72 mmol) was added in one step to a solution of 0.72 mmol of the acetylene in 20 mL of dry methylene chloride at 0 °C. After 15 min of magnetic stirring, a colorless solid precipitated. The solid was filtered off and the salt purified by crystallization from CH_2Cl_2 at low temperature. ^1H NMR (200 MHz, CD_2Cl_2) δ: 1.51 (s, *t*-Bu), 7.67 and 7.59 (multiplets, Ar). Anal. Calcd for $C_{16}H_{22}Cl_7SSb$: C, 31.18; H, 3.60. Found: C, 30.54; H, 3.52.

2-_tert_-Butyl-3-(_tert_-butyl-_d_9)-1-(4-chlorophenyl)thiirenium Hexachloroantimonate (7c) was prepared by the procedure described above, using (*tert*-butyl-d_9)-*tert*-butylacetylene, prepared with deuteriated acetone and deuteriated bromomethane.[19] ^1H NMR (200 MHz, CD_2Cl_2) δ: 1.52 (s, *t*-Bu), 7.67 and 7.59 (multiplets, Ar).

Thietium Ions. Thietium ions **8a** and **8b** are stable and can be isolated and fully characterized. The nonseparable hemideuteriated thietium ions **8c** and **8d** could also be isolated and characterized.

4-_tert_-Butyl-1,2,2,3-tetramethylthietium Hexachloroantimonate (8a). ^1H NMR (200 MHz, CD_2Cl_2) δ: 1.31 (s, *t*-Bu), 1.84 and 1.88 (singlets, 2-CH_3), 1.99 (s, 3-CH_3), 3.13 (s, 1-CH_3). Anal. Calcd for $C_{11}H_{21}Cl_6SSb$: C, 25.42; H, 4.07. Found: C, 25.06; H, 3.98.

4-_tert_-Butyl-_r_-1-(4-chlorophenyl)-2,2,3-trimethylthietium Hexachloroantimonate (8b). ^1H NMR (200 MHz, CD_2Cl_2) δ: 1.30 (s, *t*-Bu), 1.45 (s, *c*-2-CH_3), 1.98 (s, *t*-2-CH_3), 2.15 (s, 3-CH_3), 7.77 (m, Ar). ^1H NOE (200 MHz, CD_2Cl_2). *t*-Bu: {3-CH_3} 0.9. *c*-2-CH_3: {Ar} 0.9, {3-CH_3} 1.0, {*t*-2-CH_3} 0.7. *t*-2-CH_3: {*c*-2-CH_3} 0.9, {3-CH_3} nearly isochronous. 3-CH_3: {*t*-Bu} 1.7, {*t*-2-CH_3} 1.0, {*c*-2-CH_3} nearly isochronous. Ar: {*t*-Bu} 1.0, {*t*-2-CH_3} 0.9. Anal. Calcd for $C_{16}H_{22}Cl_7SSb$: C, 31.18; H, 3.60. Found: C, 30.65; H, 3.45.

4-(_tert_-Butyl-_d_9)-1-(4-chlorophenyl)-2,2,3-trimethylthietium Hexachloroantimonate (8c). ^1H NMR (200 MHz, CD_2Cl_2) δ: 1.46 and 1.99 (singlets, 2-CH_3), 2.15 (s, 3-CH_3), 7.77 (m, Ar).

4-_tert_-Butyl-1-(4-chlorophenyl)-2,2,3-tri(methyl-_d_3)thietium Hexachloroantimonate (8d). ^1H NMR (200 MHz, CD_2Cl_2) δ: 1.30 (s, *t*-Bu), 7.77 (m, Ar).

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