Nucleophilic Reactions at the Sulfur of Thiiranium and Thiirenium Ions. New Insight in the Electrophilic Additions to Alkenes and Alkynes. Evidence for an Episulfurane Intermediate

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Abstract: The thiiranium hexachloroantimonates **1a**, **3**, and **5a**−**c** and the thiirenium hexachloroantimonates **6a**−**c** and **7a** with exocyclic *S*-R substituent (R = Me, Et, *i*-Pr) react at sulfur with dialkyl disulfides R″SSR″ (R″ = Me, Et and R″ ≠ R) in CD_2Cl_2 at 25 °C to give *S*-R″ substituted ions. The reaction rates are affected by the steric hindrance of the substituents at sulfur and at ring carbons. *t*-2,*t*-3-Di-*tert*-butyl-*r*-1-methylthiiranium hexachloroantimonate (**2**) does not react, and the *t*-2-*tert*-butyl-*c*-3-phenyl-*r*-1-methylthiiranium (**5a**) reacts about 100 times faster than the *c*-2,*t*-3-di-*tert*-butyl-*r*-1-methylthiiranium ion (**1a**). The analysis of the kinetic data suggests that the sulfonium sulfur undergoes attack by the disulfide in the ring plane from a direction that is parallel to the C−C ring bond. This is also the direction which ensures the maximum overlap with the LUMO of thiiranium or thiirenium ions (determined at the RHF/3-21G*//RHF/3-21G* level). The combined consideration of the approach modality and of the maximum orbital overlap suggests that the nucleophilic substitution at sulfonium sulfur is not an S_N2-like reaction but occurs via an intermediate with episulfurane-like structure. The principle of microscopic reversibility will dictate that this is also the first intermediate in the electrophilic sulfenylation of unsaturated C−C bonds.

The electrophilic additions of halogens and sulfenyl halides to alkenes and alkynes have been extensively studied.[1,2] However, many facets of their mechanisms still wait for a complete elucidation. The main feature of these very similar processes is the stereospecific formation of anti addition products. This stereochemical course was rationalized by the intermediacy of cyclic cationic intermediates.[3] This hypothesis was then substantiated by the actual observation and isolation of haloiranium,[4] thiiranium,[5,6] and thiirenium ions.[7,8] The final anti addition products are obtained by a S_N2 mechanism, where the nucleophile attacks the ring carbons of the thiiranium or thiirenium intermediate in the ring plane and from the opposite side of the leaving group. It was also pointed out[8,9] that the opening of irenium ions by nucleophiles is a rarely observed case of nucleophilic substitution at the vinylic carbon atom occurring with inversion of configuration and with a S_N2-Vin mechanism.

Scheme 1

The mechanism of formation of thiiranium or thiirenium ions from reagents is not, as yet, fully understood, and the presence of an episulfuranic addition complex is matter of speculation (Scheme 1).[10] An old theoretical investigation suggests that in the gas phase the chlorosulfurane structure is more stable than the thiiranium chloride system,[11] whereas an isolated claim for the detection of a chloroselenurane[12] has been disproved.[13] The spectroscopic description of isolated fluorosulfuranes has not been followed by structural determinations.[14]

We have recently investigated the reaction with water of the *c*-2,*t*-3-di-*tert*-butyl-*r*-1-methylthiiranium ion (**1a**) and of the

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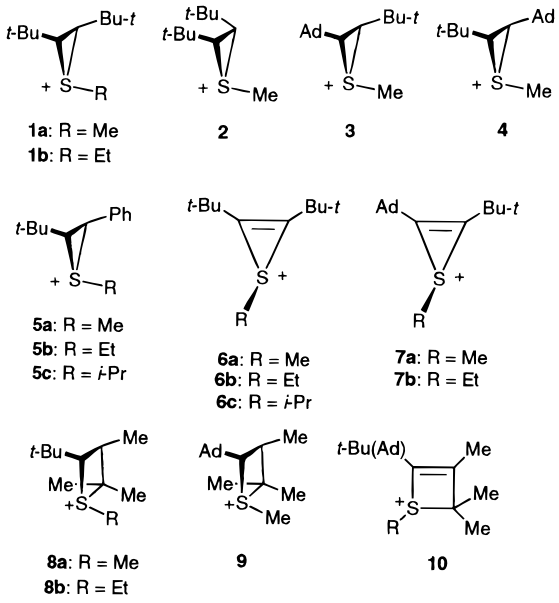
Chart 1



t-2,*t*-3 isomer **2** (Chart 1),[15] which will be named in this paper with the trivial names of trans and cis thiiranium ions. While water attacks the cis isomer **2** at the ring carbons, the attack to the trans isomer **1a** occurs exclusively at sulfonium sulfur, with the formation of (*E*)-di-*tert*-butylethylene and of protonated methanesulfenic acid. The reaction with **1a** may be considered as the reverse reaction of the electrophilic addition of the same reagent (and of a generic electrophile) to the *E* alkene. Thus, from the principle of microscopic reversibility, the study of the reactivity toward nucleophiles of stable thiiranium ions may give insights on the early steps of the electrophilic addition to alkenes. This concept may be extended to the reaction of thiirenium ions with nucleophiles and to the electrophilic addition to alkynes.

The understanding of the mechanism and of the structures of transition states and intermediates involved in the reaction shown in Scheme 1 may help to rationalize the steric and electronic parameters that direct the face selectivity in the asymmetric electrophilic addition to prochiral olefins. A possible application of this concept is offered by the recent asymmetric syntheses of sulfur- and selenium-based enantiopure electrophilic reagents.[16,17]

We present in this paper a case of nucleophilic substitution by dialkyl disulfides at the sulfonium sulfur of stable thiiranium and thiirenium ions. The reaction has been investigated both kinetically and theoretically on the basis of frontier orbital interactions to determine the most likely mechanism.

Results

We have selected for our study the reaction of weak nucleophiles, such as dialkyl disulfides, with some thiiranium and thiirenium ions carrying, at the carbon atom, bulky groups, which at the same time increase the stability of the ions and depress the possibility of nucleophilic addition to the carbon centers.

The reagents used for this research and the reaction products are listed in Chart 1. As shown in Scheme 2, the reaction of thiiranium and thiirenium ions with disulfide amounts to the replacement of the substituent at sulfur. Therefore, to monitor the reaction course, the alkyl substituents at thiiranium or thiirenium sulfur and at disulfide must be different. One exception is given by thiiranium ion **3**, with *tert*-butyl and adamantyl groups respectively cis and trans to the *S*-methyl group. The reaction with dimethyl disulfide can be followed by monitoring the formation of the isomer **4**, with cis adamantyl and trans *tert*-butyl groups. The two isomers can be easily separated and have been demonstrated not to interconvert in the absence of disulfides.[6] The reactions have been carried out in CD_2Cl_2 at 25 °C and monitored by ^{1}H NMR at regular time intervals.

The complete reaction system is reported in Scheme 2. The R″SSR″ disulfide attacks the *S*-R sulfonium sulfur of the thiiranium or thiirenium ion, generating the free olefin and the mixed R″S$^+$(SR)SR″ thiosulfonium salt. The latter can transfer to the olefin one of the "other" SR″ electrophilic group, giving the thiiranium or thiirenium ion with the *S*-R″ substituent and the mixed disulfide RSSR". This species is again able to carry out the substitution at the original thiiranium or thiirenium ion, giving rise to the disulfide RSSR. Furthermore, the fast reequilibration among the three different disulfides catalyzed by the thiosulfonium salt[18] and the competitive rearrangement of *tert*-butyl-substituted thiiranium ions to thietanium ions **8** or **9** and of *tert*-butyl-substituted thiirenium ions to thietium ions **10** have also to be considered.[6,8] Under the adopted reaction conditions (relatively high concentration of disulfide with respect to that of the substrate), only the rearrangements of trans thiiranium ions **1a,b** and **3** (with a *tert*-butyl group cis to the substituent at sulfur) to thietanium ions **8a,b** and **9** have been observed.

The thiosulfonium salts and the olefins could not be detected in the ^{1}H NMR spectra. The steady-state approximation applied to these species leads to the equations reported in Scheme 3. The differential equations related to Scheme 3 have been numerically integrated[19] and fitted to the experimental points with the Simplex procedure.[20] From the set of optimized constants provided by the Simplex procedure, we report in Table 1 the second-order rate constants k_S, describing the attack of the "symmetric" nucleophile R″SSR″.

For the sake of the following discussion, the shapes and energies of the LUMO and NLUMO with σ symmetry of thiiranium ions **1a** and **2** and of thiirenium ion **6a**, as well as the natural atomic charges at sulfur of the thiiranium and thiirenium ions listed in Chart 1, have been determined computationally ab initio at the RHF/3-21G* level, on geometries optimized at the same level.[21−23] The shapes and the energies are reported in Figure 2, while the natural atomic charges are given in Table 1.

Discussion

Effects of Substituents at Carbon and Sulfur. The analysis of the kinetic constants presented in Table 1 offers good hints

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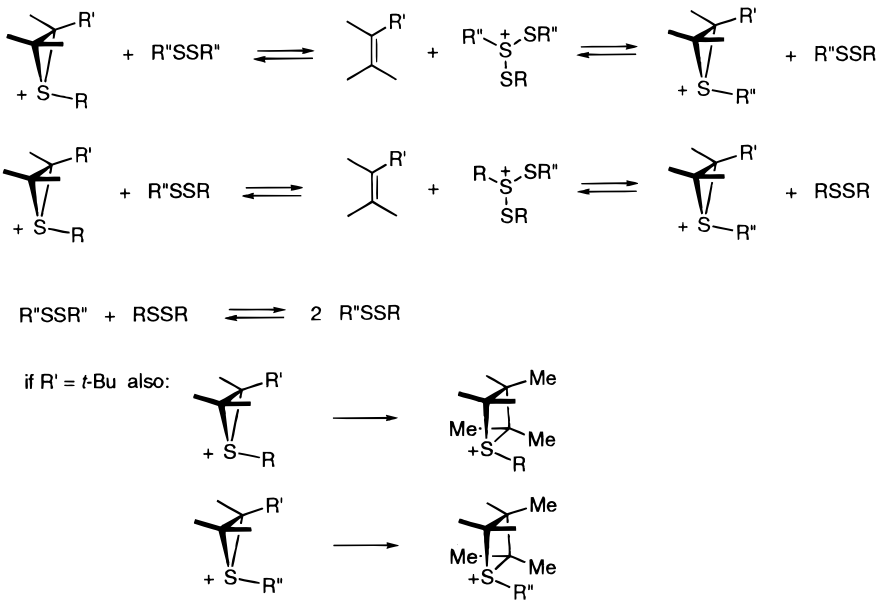
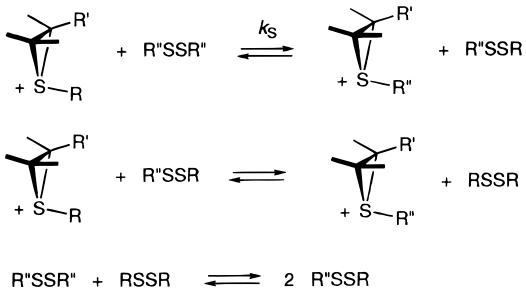
(23) The optimized geometries will be reported elsewere.

Scheme 2



Scheme 3



regarding the preferred approaching direction of the nucleophile. We will show that this preference is a decisive argument for the selection of the most likely reaction mechanism.

This discussion is based on the assumption that the reaction rates are mainly determined by the bulkiness of the substituents at sulfur and ring carbons of thiiranium and thiirenium ions. To rule out the possibility that the electrophilicity of the sulfur atom may affect the kinetic constants, the natural atomic charges at sulfur in thiiranium and thiirenium ions have been calculated ab initio at the RHF/3-21G* level. The values, reported in Table 1, do not show any meaningful correlation with the reaction rates, suggesting that electronic effects are negligible.

Because of the relatively high error in the evaluation of the kinetic constants, only differences of at least 1 order of magnitude are considered significant and will be discussed.

The steric effects exerted by the methyl and ethyl substituents at the sulfur of thiiranium ions are balanced by the reverse substitution pattern of the dialkyl disulfides, so that the rate constants are similar (cf. entries 4 and 5 and entries 7 and 8). The presence of an isopropyl group at sulfur is more effective, leading to a significant reactivity lowering both in thiiranium ions (cf. entries 5 and 6) and in thiirenium ions (entries 8 and 9). Because the natural charges at sulfur show that the isopropyl and the ethyl substituents exert similar stereoelectronic effects, the lowering must be attributed to the greater steric hindrance exerted by exocyclic isopropyl.[24]

The most significant comparison is between the reactivity of diethyl disulfide with the trans di-*tert*-butylthiiranium ion **1a** and with the cis ion **2** (entries 1 and 2): to a measurable rate for the substitution at sulfur in trans ion **1a**, there corresponds no observed substitution in cis isomer **2**. This behavior is paralleled by the nucleophilic attack of water.[15] While water reacts with sulfur in **1a**, such reaction could not be observed in **2**. The relevance of the substituents at ring carbons is also evident by the rate constant increase observed in trans thiiranium ion **5a,** with a cis-oriented phenyl substituent at carbon, when compared to the rate constant in trans thiiranium ion **1a**, with a cis *tert*-butyl group (entries 1 and 4).

As a final point, the inspection of the data in Table 1 reveals that thiirenium ions react about 2 orders of magnitude faster than thiiranium ions with the same substitution pattern (cf. entries 1 and 7 and entries 3 and 10). No correlation is found with the natural atomic charges at sulfur. The reactivity difference is explained neither by steric nor by stereoelectronic effects, but rather by the fact that the two ring systems are basically different, so that other factors may interfere. We will not further discuss this point.

Direction of Attack to Sulfonium Sulfur. The sulfonium sulfur of thiiranium and thiirenium ions can in principle be approached by the nucleophile from any direction. For the sake of this discussion we select the reciprocally orthogonal directions labeled *x*, *y*, and *z* in Figure 1.

The *x* and *y* approaches are located in the plane described by the three-member ring respectively along the direction designated by the bisector of the CSC angle and along a direction orthogonal to it. In thiiranium ions with identical and equally oriented substituents at ring carbons (as cis thiiranium ion **2**), the $+y$ approach and the $-y$ approach are equivalent, as illustrated in Figure 1a. In thiiranium ions with different substituents at ring carbons, or with differently oriented substituents, the $+y$ approach and the $-y$ approach are no longer equivalent, as evidenced in Figure 1b. A closer inspection reveals that the nucleophile is less hindered when approaching

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Table 1. Calculated Natural Atomic Charges[a] at Sulfur, Initial Concentrations, and Second-Order Rate Constants[b] for the Reaction of Disulfides with Some *tert*-Butyl-Substituted Thiiranium and Thiirenium Ions in CD_2Cl_2 at 25 °C

	thiiranium ion				disulfide		
		R	natural atomic charge at sulfur	molar concn		molar concn	k_S, $M^{-1}s^{-1}$
1	**1a**	Me	0.68	2.0×10^{-2}	EtSSEt	7.4×10^{-1}	$4.5 (\pm 0.2) \times 10^{-5}$
2	**2**	Me	0.71	2.3×10^{-2}	EtSSEt	8.8×10^{-1}	no obsd reaction
3	**3**	Me	0.74	4.9×10^{-3}	MeSSMe	3.7×10^{-1}	$2.3 (\pm 0.2) \times 10^{-5}$
4	**5a**	Me	0.64	1.7×10^{-2}	EtSSEt	1.0×10^{-1}	$4.4 (\pm 0.1) \times 10^{-3}$
5	**5b**	Et	0.70	1.7×10^{-2}	MeSSMe	1.0×10^{-1}	$1.4 (\pm 0.1) \times 10^{-3}$
6	**5c**	*i*-Pr	0.68	1.8×10^{-2}	MeSSMe	4.6×10^{-1}	$5.9 (\pm 0.2) \times 10^{-5}$
	thiirenium ion				disulfide		
		R	natural atomic charge at sulfur	molar concn		molar concn	k_S, $M^{-1}s^{-1}$
7	**6a**	Me	0.71	1.7×10^{-2}	EtSSEt	3.3×10^{-2}	$1.5 (\pm 0.2) \times 10^{-3}$
8	**6b**	Et	0.78	2.2×10^{-2}	MeSSMe	3.9×10^{-2}	$3.8 (\pm 0.4) \times 10^{-3}$
9	**6c**	*i*-Pr	0.72	3.0×10^{-2}	MeSSMe	1.2×10^{-1}	$7.8 (\pm 0.3) \times 10^{-5}$
10	**7a**	Me	0.70	1.8×10^{-2}	EtSSEt	3.8×10^{-2}	$4.4 (\pm 0.4) \times 10^{-3}$

[a] Calculated ab initio at the 3-21G*//3-21G* level. [b] Average and standard deviation from three experiments.

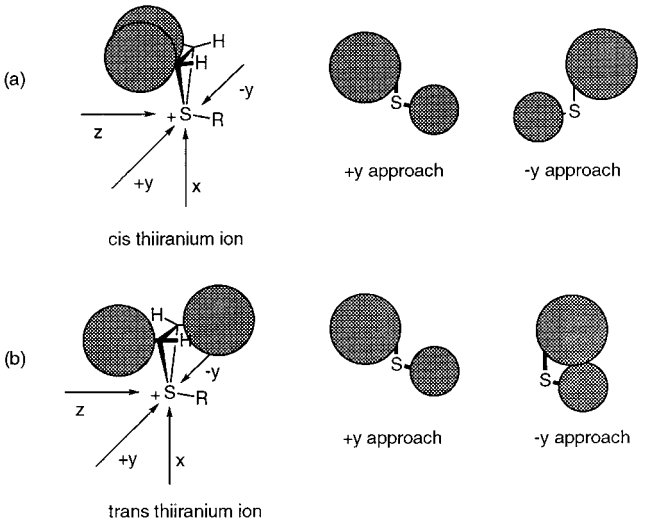

Figure 1. Orthogonal approaching directions of the nucleophile to the sulfonium sulfur of (a) cis substituted and (b) trans-substituted-thiiranium ions.

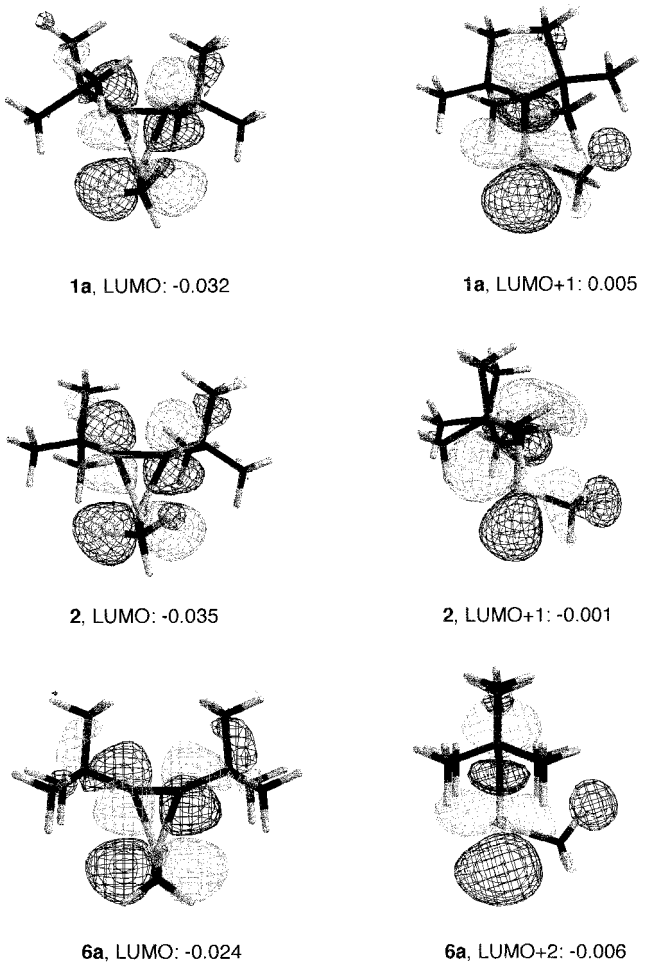

Figure 2. Shapes and eigenvalues (hartree) of LUMO and LUMO+1 of thiiranium ions **1a** and **2** and of LUMO and LUMO+2 of thiirenium ion **6a**, calculated ab initio at the 3-21G*//3-21G* level.

along the $-y$ direction, where the substituents at carbon and at sulfur are on the same side of the ring, than along the $+y$ direction, where the substituents are on the opposite sides of the ring.

The approach along the *z* direction occurs from a direction orthogonal to the molecular plane and from the opposite side to the exocyclic substituent at sulfur. It should be considered that in these ions the exocyclic C−S bond is almost perpendicular to the plane containing the ring.[25]

The results outlined in the preceding paragraph show that the nucleophile attack is sensitive to the substitution pattern both at sulfur and at ring carbons. We can therefore rule out the *z* approach, which cannot be influenced by the hindrance of the substituent at sulfur, and the *x* approach, which is insensitive to the substituent pattern at the ring carbons. Only the $+y$ and the $-y$ approaches may be affected by the hindrances of the complete substitution pattern. If we assume these as the exclusive approaching directions (and electronic factors, illustrated in the next paragraph, will substantiate this assumption), then the set of kinetic constants in Table 1 can be comprehensively rationalized. With reference to Figure 1, the two $+y$ and $-y$ approaches are both sterically hindered in the case of cis thiiranium ion **2**, and this explains why this ion is unreactive toward disulfide. On the other hand, the $-y$ approach of trans thiiranium ion **1a** is decidedly less hindered than the

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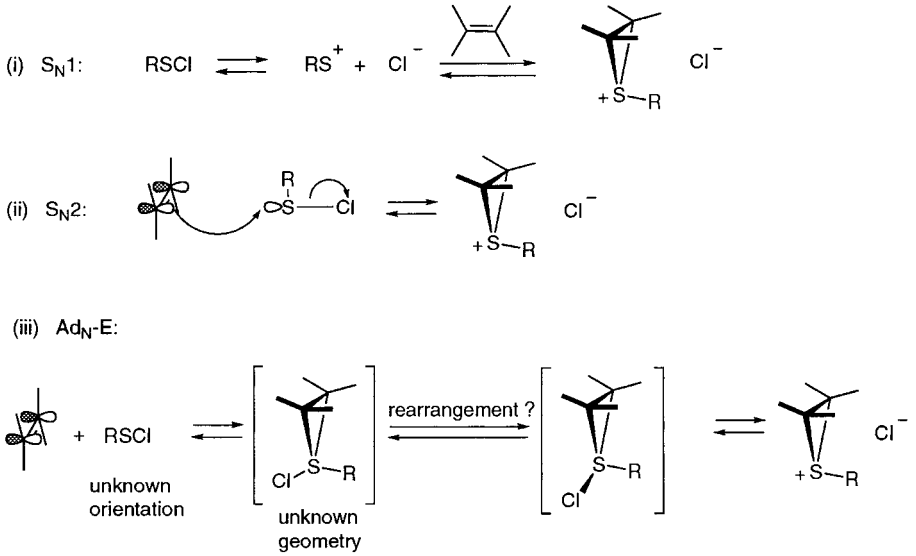
Scheme 4



$+y$ approach, so that the attack of disulfide may occur along the $-y$ direction. Only the approach along the $-y$ direction explains why the attack to thiiranium ions **5a** and **5b** (with a cis-oriented phenyl substituent at one ring carbon) is so much faster than the attack to thiiranium ions **1a** and **3** (with a cis-oriented *tert*-butyl substituent). A nucleophile approaching along the $+y$, x, or z direction of the four thiiranium ions **1a**, **3**, and **5a**,**b** would be subjected to steric effects almost to the same degree.

Symmetry Properties of LUMO and NLUMO of Thiiranium and Thiirenium Ions. The LUMOs of di-*tert*-butyl-substituted thiiranium ions **1a** and **2** and thiirenium ion **6a**, calculated ab initio at the 3-21G*//3-21G* level and reported in Figure 2, are Walsh-type orbitals of b_2 symmetry (apart from small local perturbations in **1a** and **2**, due to the different orientations of the *tert*-butyls). These orbitals present the greatest extension around the sulfur atom and along the y direction and offer the greatest interaction with an occupied orbital of the nucleophile when this latter approaches exactly along this direction. This interaction, between an occupied orbital of the nucleophile with the LUMO of the electrophile, is energy-gap controlled.

The next vacant orbital with σ symmetry is the NLUMO (LUMO+1) in the case of thiiranium ions **1a** and **2** and the LUMO+2 in the case of thiirenium ion **6a**. These orbitals, which are of a_1 symmetry (with local perturbations originating from the substituents at sulfur and ring carbons), display the greatest extension along the x direction. The interaction with a nucleophile approaching along this direction will be predominant (orbital-overlap control) only if a particularly favorable orbital overlap overcomes the LUMO interaction with the nucleophile in the y direction. Our kinetic data, which point to an approach along the y direction, indicate that the nucleophilic attack to sulfur of thiiranium and thiirenium ions is dominated by the energy-gap control.

Mechanism of Electrophilic Addition to Unsaturated C−C Bond. The first step of the electrophilic addition of sulfenyl chlorides to alkenes or alkynes may also be regarded as the nucleophilic attack of the unsaturated C−C bond to the sulfur atom of sulfenyl chloride. As such, the principle of maximum overlap between the HOMO of the nucleophile, i.e., the symmetric π orbital, and the LUMO of the electrophile will dictate the symmetrical approach of the electrophile (i.e., equidistant from the two unsaturated C atoms). In analogy with the nucleophilic substitution at the sp^3 carbon, the three classical mechanisms, S_N1, S_N2, and Ad_N-E will be discussed in connection with the substitution at sulfur.[26] The three mechanisms are shown in Scheme 4 and may be outlined as follows: (i) S_N1, with rate-determining unimolecular heterolysis of the S−Cl bond; (ii) S_N2, with concerted approach of the π cloud of the unsaturated C−C bond and detachment of the chloride ion; (iii) Ad_N-E, with the intermediacy of sulfuranic species, which may be considered the mechanistic analogue of the Meisenheimer intermediate[27] (for the nucleophilic addition to aromatic rings) or of the anionic tetrahedral intermediate[28] (for the nucleophilic addition to C−C double bonds).

The S_N1 process implies the generation of the sulfenium cation. However, species that can be assigned to the structure of a RS^+ ion have been detected only in the gas phase and only in the case of aromatic sulfenium ions.[29] Any attempt to generate these ions in a condensed medium has always led to species where the RS^+ moiety is associated with a carrier. Thus the action of strong Lewis acids ($AgBF_4$ or $SbCl_5$) on sulfenyl halides generates chlorosulfonium ions, which may be described as sulfenium ions carried by sulfenyl chloride molecules.[30] For these reasons we are inclined to exclude the possibility of a nonconcerted S_N1 process.[31]

As in the case of nucleophilic substitution at the sp^3 carbon, the S_N2 mechanism requires strict limitations to the entering direction of the nucleophile, the π electrons of the double bond: the approach must occur along the direction of the S−Cl bond and from the side opposite to the leaving group. If the addition of sulfenyl chloride to an unsaturated C−C bond follows this mechanism, and because the "product" is generated in one step, the principle of microscopic reversibility requires

(26) IUPAC recommends the designators D_N+A_N, A_ND_N, and A_N+D_N for the S_N1, S_N2, and Ad_N-E mechanisms, respectively. Guthrie, R. D.; Jencks, W. P. *Acc. Chem. Res.* **1989**, *22*, 343.

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(30) Capozzi, G.; Lucchini, V.; Modena, G.; Rivetti, F. *J. Chem. Soc., Perkin Trans. 2* **1975**, 361.

(31) A stable sulfenium ion, with a sulfur atom protected toward nucleophiles by a cage, has been recently isolated and characterized: Kobayashi, K.; Sato, S.; Horn, E.; Furukawa, N. *Tetrahedron Lett.* **1998**, *39*, 2593.

that the nucleophilic substitution by chloride ion to the sulfonium sulfur of the "product" (thiiranium or thiirenium ion) will occur along the same direction traveled by the leaving group (the chloride ion) in the forward reaction. Thus, according to this mechanism, the entering direction of chloride ion, or of any other nucleophile, to the sulfur atom of thiiranium and thiirenium ions must be the *x* direction shown in Figure 1. The kinetic data in Table 1 and the considerations based on orbital interaction exclude the probability of this approaching direction. The exclusion of the *x* approach is particularly important, as it rules out the S_N2 mechanism in the nucleophilic substitution to sulfonium sulfur and hence, for the principle of microscopic reversibility, also the S_N2 mechanism for the nucleophilic substitution at the sulfenyl halide by the C−C unsaturated bond.

The Ad_N-E mechanism requires an intermediate, which may be described as an episulfurane species. We have already outlined in the Introduction that, although episulfuranes have been proposed as "first" intermediates in the addition of sulfenyl chlorides to alkenes and alkynes,[10] their existence has never been demonstrated.[11−14] The addition of a nucleophile to thiiranium or thiirenium ions along the less hindered *y* direction may generate an episulfurane structure, which has the characteristics of an intermediate and cannot be considered a S_N2 transition state, because the direction of the entering group and the detachment direction of the leaving group (the C−C moiety) are far from collinearity (the two directions are approximately orthogonal). Thus, the *y* approach requires the intermediacy of a discrete species and is therefore compatible with the Ad_N-E mechanism only.

Conclusions

The LUMO of thiiranium and thiirenium ions, with b_2 symmetry, enjoys the greatest interaction (under energy-gap control) with an occupied orbital of the disulfide nucleophile when this latter approaches along the *y* direction (Figure 1). The interaction leads to the formation of an episulfurane intermediate, implying the occurrence of the Ad_N-E mechanism. The LUMO+1 of thiiranium ions or the LUMO+2 of thiirenium ions, with a_1 symmetry, have the greatest interaction (under orbital-overlap control) with the nucleophile approaching along the *x* direction. This direction is collinear with the detachment direction of the C−C unsaturated bond as leaving group. The reaction will therefore occur with a S_N2 mechanism.

The comprehensive consideration of the kinetic data reported in Table 1 points to the *y* approaching direction and therefore to the Ad_N-E mechanism and to the intermediacy of an episulfurane species. It is of course conceivable that the episulfurane intermediate, as a discrete species, can undergo some degree of rearrangement along the reaction coordinate. The principle of microscopic reversibility suggests the geometry of the episulfurane structure directly derived from the addition of chloride ion to thiiranium or thiirenium ion but cannot give any hint regarding the eventual rearrangement of this structure and the reciprocal orientation of alkene or alkyne and of sulfenyl chloride during the first step of the electrophilic addition to the unsaturated C−C bond (cf. Scheme 4).

Experimental Section

General. Melting points are uncorrected. ^{1}H NMR spectra were recorded at 200 MHz or at 250 MHz, ^{13}C NMR at 62.9 MHz, using CD_2Cl_2 or liquid SO_2 as solvent. The NMR instruments are equipped with a variable-temperature control unit, and all the kinetic measurements were obtained at 25 °C. Commercial CD_2Cl_2 was carefully anhydrified before use with A4 molecular sieves. 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.

Kinetic Measurements. The concentrations of the reagents in CD_2Cl_2 have been determined by comparison of the integrated areas of appropriate resonances with that of the proton impurity of the solvent. The concentration of the impurity has been previously measured by comparison with the signal of 1,4-dinitrobenzene, at a concentration determined by weighing. The reactions have been monitored, at regular intervals of time, using NMR tubes equipped with airtight screw caps. To compensate for the varying spectrometer conditions, the monitored intensities were normalized against their sum. The differential equations in Scheme 3 have been numerically integrated[19] and fitted to the normalized concentrations with the Simplex procedure.[20]

General Synthesis of Reagents. The hexachloroantimonates of ethyl and isopropyl alkylbis(alkylthio)sulfonium salts have been prepared similarly to the methyl analogue.[32] The thiiranium and thiirenium ions have been prepared from the corresponding alkenes or alkynes and the appropriate thiosulfonium hexachloroantimonates following the already reported procedures.[6,8] The spectral characteristics of thiiranium and thiirenium hexachloroantimonates **1a**−**4** and **6a** and of thietanium hexachloroantimonates **8a** and **9** are reported elsewhere.[6,8]

Ethylbis(ethylthio)sulfonium Hexachloroantimonate. Prepared in 75% yield as a viscous oil. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.61 (9H t, J = 7.3); 3.52 (6H, broad q, J = 7.3).

Isopropylbis(isopropylthio)sulfonium Hexachloroantimonate. Obtained in 78% yield as an oil. ^{1}H NMR (250 MHz, CD_2Cl_2): δ 1.60 (18H, d, J = 6.6), 3.89 (3H, broad m).

***c*-2,*t*-3-Di-*tert*-butyl-*r*-1-ethylthiiranium Hexachloroantimonate (1b).** ^{1}H NMR (250 MHz, CD_2Cl_2): δ 1.18 (9H, 3-*t*-Bu, s), 1.35 (9H, 2-*t*-Bu, s), 1.68 (3H, 1-Me, broad t, J = 7.3), 3.16 (1H, 1-CH_2, m), 3.33 (1H, 1-CH_2, m), 3.80 (1H, 2-H, d, J = 13.4), 4.04, (1H, 3-H, d). ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ 14.26, 27.26, 29.32, 31.81, 33.03, 35.09, 72.27, 72.83. Anal. Calcd for $C_{12}H_{25}Cl_6SSb$: C, 26.9; H, 4.7; S, 6.0. Found: C, 26.8; H, 4.4; S, 5.7.

***t*-2-*tert*-Butyl-*c*-3-phenyl-*r*-1-methylthiiranium Hexachloroantimonate (5a).** ^{1}H NMR (250 MHz, CD_2Cl_2): δ 1.29 (9H, s, *t*-Bu), 2.16 (3H, s, Me), 4.38 (1H, 2-H d, J = 12.0), 5.56 (1H, 3-H, d); 7.60−7.76 (5H, Ph, m). The orientation of the *tert*-butyl and phenyl groups and the assignment of the ring protons have been determined with differential NOE spectroscopy.[33] The results are reported as follows: observed nucleus: {perturbed nucleus}, % enhancement. ^{1}H NOE (200 MHz, CD_2Cl_2): *t*-Bu: {3-H}, 0.8; Me: {2-H}, 1.5; {Ph, *o*-H}, 0.9; 2-H: {*t*-Bu}, 10.8; {Me}, 3.7; {Ph, *o*-H}, 8.6; 3-H: {*t*-Bu}, 18.0; {Me}, 0.6; {2-H}, 1.4; {Ph, *o*-H}; Ph, *o*-H: {Me}, 0.9; {2-H}, 2.9; {3-H}, 1.7. ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ 16.67, 27.15, 33.59, 66.05, 71.37, 122.80, 130.65, 131.62, 133.94. Anal. Calcd for $C_{13}H_{19}Cl_6SSb$: C, 28.8; H, 3.5; S, 5.9. Found: C, 27.8; H, 3.5; S, 5.6.

***t*-2-*tert*-Butyl-*c*-3-phenyl-*r*-1-ethylthiiranium Hexachloroantimonate (5b).** ^{1}H NMR (250 MHz, CD_2Cl_2): δ 1.28 (9H, *t*-Bu, s), 1.33 (3H, Me, t, J = 7.5), 2.47 (2H, CH_2, m), 4.36 (1H, 2-H, d, J = 11.8), 5.58 (1H, 3-H, d), 7.60−7.75 (5H, Ph, m). ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ 12.08, 27.19, 29.68, 33.25, 66.50, 69.11, 123.22, 130.62, 131.33, 133.79. Anal. Calcd for $C_{14}H_{21}Cl_6SSb$: C, 30.2; H, 3.8; S, 5.8. Found: C, 29.8; H, 3.7; S, 5.5.

***t*-2-*tert*-Butyl-*c*-3-phenyl-*r*-1-isopropylthiiranium Hexachloroantimonate (5c).** ^{1}H NMR (250 MHz, CD_2Cl_2): δ 1.13 (3H, 1-Me, d, J = 6.9), 1.27 (9H, *t*-Bu, s), 1.60 (3H, 1-Me, d, J = 6.9), 2.44 (1H, 1-H, heptet), 4.35 (1H, 2-H, d, J = 11.8), 5.59 (1H, 3-H, d), 7.60−7.76 (5H, Ph, m). ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ 20.70, 22.08, 27.26, 33.06, 44.26, 66.62, 68.46, 123.28, 130.71, 131.17, 133.78. Anal. Calcd for $C_{15}H_{23}Cl_6SSb$: C, 31.6; H, 4.1; S, 5.6. Found: C, 30.0; H, 4.0; S, 6.0.

2,3-Di-*tert*-butyl-1-ethylthiirenium Hexachloroantimonate (6b). ^{1}H NMR (250 MHz, liquid SO_2): δ 1.48 (3H, 1-Me, t, J = 7.6), 1.55

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(18H, *t*-Bu, s), 2.95 (2H, 1-CH_2, q). ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ 10.98, 28.16,33.28, 40.14, 114.98. Anal. Calcd for $C_{12}H_{23}Cl_6SSb$: C, 27.0; H, 4.3; S, 6.0. Found: C, 26.9; H, 4.2; S, 5.9.

2,3-Di-*tert*-butyl-1-isopropylthiirenium Hexachloroantimonate (6c). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 1.47 (6H, 1-Me, d, J = 6.9), 1.50 (18H, *t*-Bu, s), 3.25 (1H, 1-H, heptet). ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ 19.68, 28.58, 33.09, 47.33, 115.86. Anal. Calcd for $C_{13}H_{25}Cl_6SSb$: C, 28.5; H, 4.6; S, 5.8. Found: C, 28.3; H, 4.2; S, 5.4.

2-Adamantyl-3-*tert*-butyl-1-methylthiirenium Hexachloroantimonate (7a). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 1.51 (9H, *t*-Bu, s), 1.7−2.3 (15H, adamantyl, m). ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ 27.47, 27.94, 30.39, 33.45, 35.09, 35.39, 39.89, 113.64, 113.87. Anal. Calcd for $C_{17}H_{27}Cl_6SSb$: C, 34.1; H, 4.5; S, 5.4. Found: C, 33.5; H, 4.5; S, 5.4.

2-Adamantyl-3-*tert*-butyl-1-ethylthiirenium Hexachloroantimonate (7b). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 1.46 (3H, 1-Me, t, J = 7.6), 1.50 (9H, *t*-Bu, s), 1.7−2.3 (15H, m, adamantyl), 2.93 (2H, 1-CH_2, q). ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ 11.04, 27.56, 28.23, 33.18, 34.81, 35.39, 40.20, 40.37, 113.94, 114.06. Anal. Calcd for $C_{18}H_{29}Cl_6SSb$: C, 35.3; H, 4.8; S, 5.2. Found: C, 34.2; H, 4.7; S, 4.9.

***t*-4-*tert*-Butyl-*r*-1-ethyl-2,2,*c*-3-trimethylthietanium Hexachloroantimonate (8b).** ^{1}H NMR (250 MHz, CD_2Cl_2): δ 1.12 (9H, *t*-Bu, s), 1.28 (3H, 3-Me, d, J = 6.5), 1.56 (3H, 1-Me, m), 1.80 (6H, 2-Me_2, bs), 3.14 (1H, m), 3.39 (1H, m), 3.63 (1H, m), 3.76 (1H, 4-H, broad d, J = 11.3). ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ 11.62, 16.61, 19.21, 27.03, 30.24, 33.53, 36.53, 44.25, 66.22, 72.92. Anal. Calcd for $C_{12}H_{25}Cl_6SSb$: C, 26.9; H, 4.7; S, 6.0. Found: C, 26.7; H, 4.5; S, 5.8.

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