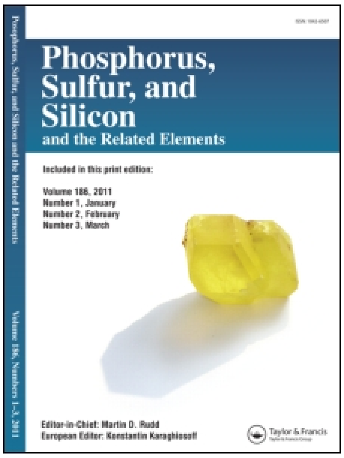

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Thiiranium and Thiirenium Ions Chemistry and Stereochemistry

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THIIRANIUM AND THIIRENIUM IONS CHEMISTRY AND STEREOCHEMISTRY

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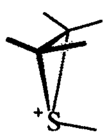
The role of thiiranium and thiirenium ions in the electrophilic additions to alkenes and alkynes and the corresponding inverse reactions, are revisited also in the light of the recently reported rearrangements on some of these cations. The occurrence of S_N2-Vin mechanism is discussed on the basis of the available experimental evidence and of quanto mechanical computation. Preliminary results on the reactivity of some stable thiiranium ions as a function of substitution pattern and on the enantioselective bifunctionalization of alkene via an optically active thiiranium ion are also reported.

Key Words thiiranium ions, thiirenium ions, anionotropic rearrangements, S_N2-Vin mechanism, optically active thiiranium ions, asymmetric synthesis.

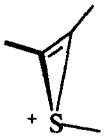
A focal point of Physical Organic Chemistry of the last decades has been the characterization and eventually the isolation of the cationic intermediates in either the solvolysis of alkyl substrates or the electrophilic additions to π systems: *i.e.* classic and bridged carbonium ions, halonium, sulfonium ions, etc.[1]

Their detection by physical methods, mainly by NMR methodologies, or their isolation as stable species confirmed beyond any doubt the mechanistic hypothesis which predicted their presence and their role along the reaction coordinate with that allowing a deeper understanding of the processes.[2]

Among these species a specific place is occupied by thiiranium and thiirenium ions **1** and **2**.

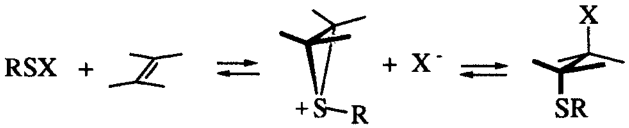


1



2

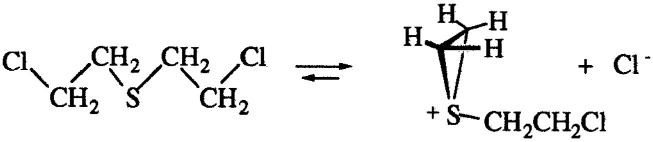
The former, **1**, is the intermediate of the electrophilic additions of sulphenyl halides to alkenes[3] and of the solvolysis of β-thioalkyl halides, and of related reactions[4] (Eq. 1).



(1)

The role of the β-sulfur in assisting the unimolecular solvolysis of β-thioalkyl halides (Eq. 1 from right to left) was recognized very early[5] and it is one of the most typical example of anchimeric assistance to, or neighboring group participation in, solvolysis. The rate enhancement observed may be as high as eight powers of ten.[6]

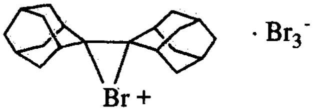
Indeed, the deadly mustard gas, that has the formula below reported, has a tremendous alkylating power thought to be due to the thiiranium ion, which is the initial rather stable intermediate of the solvolytic reaction.[7]



(2)

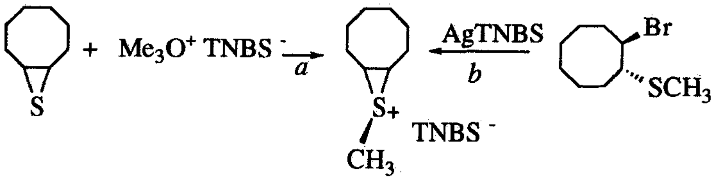
The bridged structure of the intermediate in the electrophilic addition of sulphenyl halides to alkenes,[8] (Eq. 1 from left to right), was also suggested since the beginning of these studies because of the strict anti stereoselectivity of these reactions, following the earlier Roberts' proposal[9] of bromonium ion intermediate to explain the stereochemistry of alkene bromination.

However, contrary to bromonium ions, which have been detected by physical methods only in a few cases and isolated as stable species in one case only (the one formed from the very hindered adamantylideneadamantano[10] **3**), thiiranium ions are much more stable compounds which have been observed and isolated in a large number.[3]



3

The first thiiranium ion isolated as stable salt has been the *cis*-cyclooctane-*S*-methyl-thiiranium 2,4,6-trinitrobenzenesulfonate, that has been prepared either by methylation of the thioepoxide[11a] of the *cis*-cyclooctene (path *a* in Eq. 3) or by reaction of the *trans*-1-chloro-2-methylthiocyclooctane with silver trinitrobenzenesulfonate[11b] (path *b* in Eq. 3).

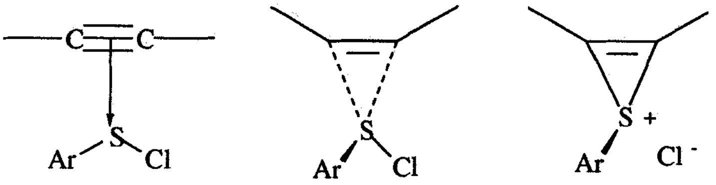


(3)

TNBS = 2,4,6-trinitrobenzenesulfonate

Other thiiranium ions have been prepared as stable salts either by similar approaches or by reaction of the appropriate alkene with sulfenyl halides in the presence of the silver salts of non nucleophilic anions[12-14] (see Eq. 1 where X = BF_4, $SbCl_6$, etc.).

The history of thiirenium ion **2** is rather shorter.[3a,14] It begun with the pioneering studies of sulphenyl halide addition to alkynes by N. Kharash in the early fifties,[15] which showed that the addition is anti stereoselective. This was explained postulating that the electrophile covers one side of the molecule forming some kind of complex (Scheme 1).[16]



SCHEME 1

The reluctance to propose the intermediate thiirenium ion structure was due to the fact that the three membered ring should have an antiaromatic character, because of the four electrons in an unsaturated three membered cycle, and hence be very unstable.

Further informations on the nature of the cationic intermediate was obtained when the introduction of the so called "super leaving groups" (trinitrobenzenesulphonates, triflates, etc.) allowed the studies of the unimolecular solvolysis of vinyl derivatives which were generally described as in Equation (4).[17]

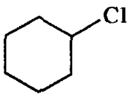
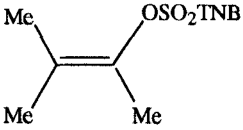
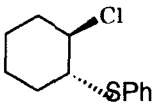
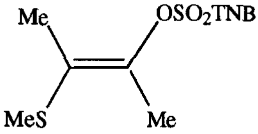
(4)

LG = 2,4,6-$(NO_2)_3$-C_6H_2-SO_3; CF_3-SO_3; FSO_3; etc.

It was in fact observed that the β-thio group had much the same effect that it has in the solvolysis of β-thioalkyl chlorides. Indeed anchimeric effects of the order of about 10^4 were observed for both classes of compounds (Table I).[4,18] Consequently the cationic intermediate should be a bridged ion

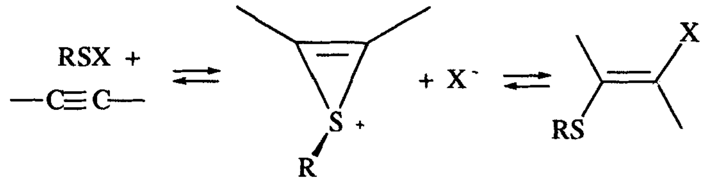
TABLE I

Relative rates of solvolyses of selected substrates.

	k_{rel}	Ref.		k_{rel}	Ref.
	1^{a}	4		1^{b}	18
	$7 \times 10^{4\,a}$	4		$4 \times 10^{4\,b}$	18

a. in 80% ethanol at 118 °C. *b*. in nitromethane:methanol, 9:1, at 25°C.

It is therefore possible to describe this system with the general Equation 5 which may be read from left to right as well as from right to left, similarly to that proposed for the reaction of sulfenyl chlorides with alkenes (Eq. 1).

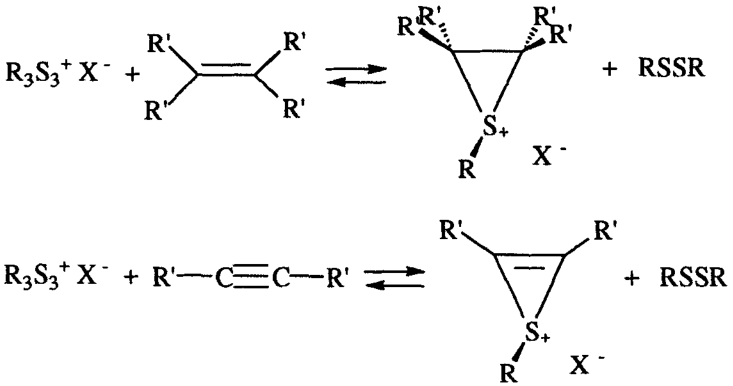


(5)

At about the same time, computational studies[19] showed that the bridged thiirenium ion could be a stable specie, more stable that the isomeric open β-tiovinyl cation. They also predicted that the sulfur is highly pyramidal (about 98 degrees with respect to the ring plane) with a very high energy barrier for pyramidal inversion (73 kcal/mol). Thus the lone pair at sulfur is pushed away from the molecular plane, with the consequence of a strong reduction of the antiaromatic character of the molecule.

Also in the same years efforts to obtain some thiirenium salts were done. The early approaches, based on the reactions of β-thiovinyl halides with silver salts of appropriate acids met with severe difficulties because of the presence of other nucleophilic centers in the molecule. However this difficulty was overcome by the introduction of a novel family of reagents: the alkyl(bisalkythio)- or aryl(bisarylthio)sulfonium salts (Scheme 2).[20]

$$RSSR + RSCl + AgX \longrightarrow R_3S_3^+ + X^- + AgCl$$



SCHEME 2

They transfer very efficiently the RS^+ residue to the triple bond[21] (see Scheme 2), and also to a double bond,[12a,22] leaving behind the very poorly nucleophilic disulfide, which usually does not interfere with the reaction.

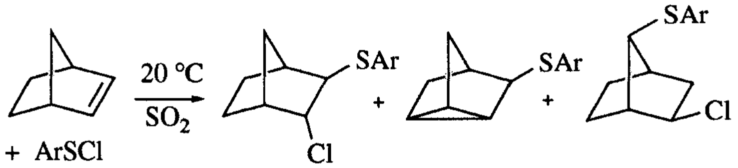
By this approach several thiirenium ions could be prepared and characterized by NMR and quite a few isolated as stable salts. Among them di-*tert*-butyl-*S*-methyl thiirenium tetrafluoborate (**4**) and hexachloroantimonate were prepared and found to be rather stable.[21] They have been subjected to an accurate X-ray analysis at -100 °C;[23] it was rewarding to find a good correspondence between the experimental structural parameters and those found by *ab-initio* calculations.[19]

These early studies cleared a few points: i) thiiranium and thiirenium ions are rather stable species; ii) their stability depends strongly on the substitution pattern: alkyl (but not aryl) substitutions at ring carbons stabilize the ions; iii) substituent at sulfur acts *via* inductive effect so that alkyl substituents are better than aryl substituents.[3a]

Moreover, it was firmly established that Equations 1 and 5 describe correctly the reaction of sulfenyl derivatives with alkenes and with alkynes respectively: *i.e.* both reactions, under appropriate conditions, are fully reversible, both have bridged ions as intermediates.[24]

The access to thiiranium and thiirenium ions allows to study their reactivity as isolated species and hence, at least in principle, to measure and compare the different rates of the different reaction paths.

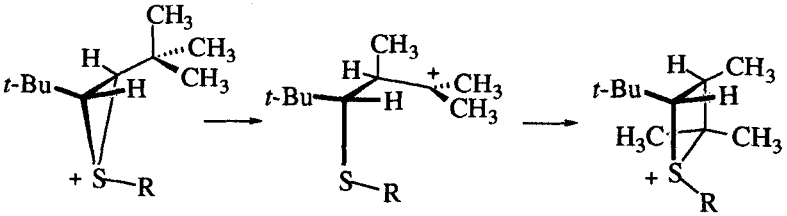
One of the puzzling points of the addition of sulfenyl chlorides to strained alkene, as for example norbornene, was that, depending on the individual reagent and on the reaction conditions, products of simple additions and products derived by skeleton rearrangements were observed (Scheme 3).[25]



Ar = 2,4-$(NO_2)_2$-C_6H_3-

SCHEME 3

A step forward in understanding these reactions was made with the detailed study of the rearrangements of 2-*c*,3-*t*-di-*tert*-butyl-*S*-methylthiiranium ion **5** to the thietanium ion **6**.[26] The reaction has been studied in detail and the results are summarized in Scheme 4.



5 **6**

R = Me: $k_{cis} = 7.42 \times 10^{-6}\ s^{-1}$ $k_H/k_D = 1.27$

$k_{trans} = 3.83 \times 10^{-7}\ s^{-1}$

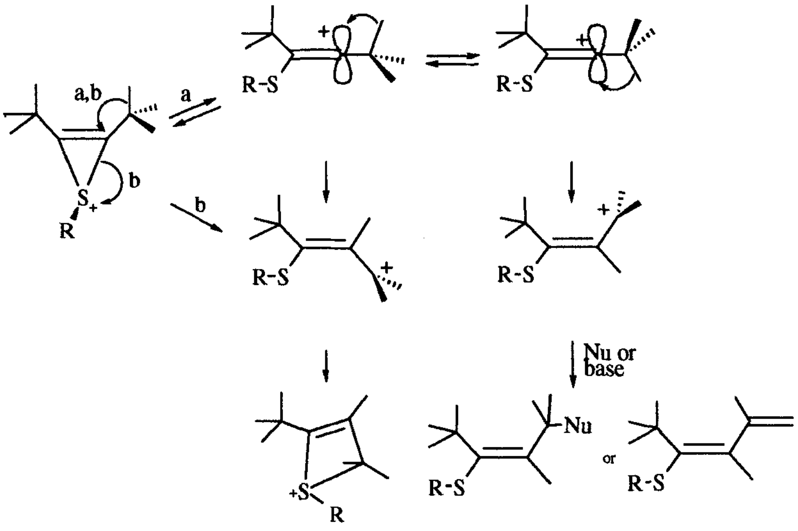
R = 4-Cl-C_6H_4 $k_{cis} = 2.83 \times 10^{-3}\ s^{-1}$

SCHEME 4

The main points are: i) the rearrangement is concerted, *i.e.* the S-C bond breaking is anchimerically assisted by the methyl shift, as it is shown by the stereochemistry of **6** and by the KIE measured on thiiranium ion **5** perdeuterated at one tert-butyl group, in a process that can be visualized as an internal S_N2 reaction; ii) the methyl shift from the tert-butyl group cis to the *S*-methyl is faster than that from the trans position. It corresponds to the fact emerging from *ab-initio* computation that there is a significant non bonding interaction between the two groups;[27] iii) the reaction with the homologous *S*-4-chlorobenzenethiiranium ion is ca. 350 times faster.

Beside the intrinsic interest of these findings, this rearrangement has several consequences: i) the large increase of reaction rate by the substitution of the *S*-methyl with *S*-aryl group confirms the qualitative observation of the different reactivity of sulfenyl derivatives as a function of the substituent at the sulfur. ii) the rearrangements, some time extensive, observed in the addition of sulfenyl halides to strained policyclic alkenes likely occur by a similar mechanism. They do not require different intermediates, as it had been suggested, simply they occur at different rates depending on the particular structure.[24] iii) the kind and the extent of the rearrangements observed may simply derive by the ratios between the rates of rearrangement and the rates of attack by the nucleophiles present in the reaction media on the various electrophilic centers.

We also observed, with some surprise, that the di-*tert*-butyl-thiirenium ions **4** undergoes to the same kind of rearrangement.[28] The results are summarized in Scheme 5.



R = Me $k = 6.30 \times 10^{-8}\ s^{-1}$ $k_H/k_D = 1.19$
$R = 4\text{-}Cl\text{-}C_6H_4$ $k = 3.93 \times 10^{-8}\ s^{-1}$

SCHEME 5

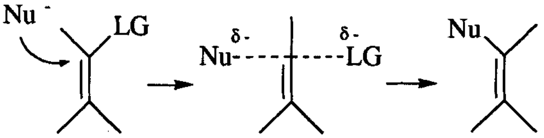
It should be noticed that similar rate enhancements are observed on thiiranium and thiirenium ions by substitution of the *S*-methyl with the *S*-aryl group and the substantially slower reaction of the thiirenium ions with respect to the saturated counterpart. Very likely the steric compression present in **5** but not in **4** is, largely, responsible of this fact. Indeed the reactivity ratio is smaller if the comparison is made with the rearrangement rate from the *trans*-*tert*-butyl of **5**.

The study of this rearrangement called again for our attention on the problem of nucleophilic substitution at vinyl carbon.

It had been pointed out by Rappoport[29] and by us[14] that the anchimeric assistance exerted by sulfur in the unimolecular solvolysis of β-thio vinyl derivatives as well as the nucleophilic attack on thiirenium ions amounts to a kind of S_N2 reaction.

With reference to Scheme 5, the only observed product is that derived by path *b*, while products expected by path *a* are not observed. Furthermore a significant KIE is observed in the substrate perdeuterated at one *tert*-butyl group. The rearrangement observed is definitely a concerted process occurring with inversion of configuration at the ring vinyl carbon. Therefore it corresponds to a nucleophilic substitution occurring with a mechanism which can be named S_N2-Vin mechanism, the logical analogue of the aliphatic S_N2 mechanism.

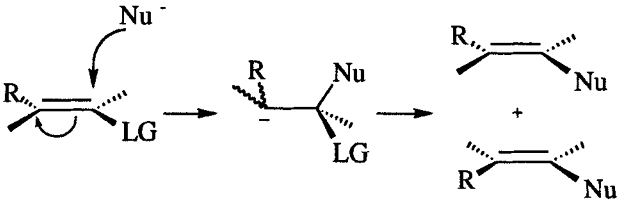
S_N2-Vin mechanism



SCHEME 6

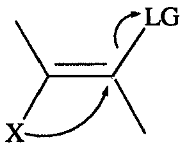
These reactions can be considered an exception to the general rule that nucleophiles exclusively attack the sp^2 carbon from a direction perpendicular to the molecular plane,[30] leading to retention of configuration or stereoconvergence (Ad_N-E mechanism). This rule is indeed based on an extremely large number of investigations on a variety of substrates and is also supported by some theoretical studies.

Ad_N-E mechanism



SCHEME 7

On the other hand the two exceptions refer to rather special cases: the thiirenium ion ring formation is a reaction in which the sulfur is stereochemically constrained to attack the vinyl carbon in the molecular plane (system **8**), while the nucleophilic attack on thiirenium ion (system **9**) is also somewhat atypical because of the assumed extreme instability of thiirenium ions.



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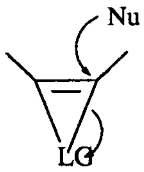


9

Furthermore, revising the literature with a more critical eye, it emerged that there are quite a few other cases where substitution at a vinyl carbon may occur with inversion of configuration, implying the intervention of the S_N2-Vin mechanism.

We are addressing the problem by two approaches: i) a theoretical study of some models, aimed at the search for possible correlations between the orbital characteristics of the electrophile and the stereochemistry of the substitution reactions; ii) an experimental study of some nucleophilic reactions on isolated thiiranium and thiirenium ions.

The Relevance of the LUMO of the Electrophile in Vinyl Substitutions. The factors which determine the mode of reaction of a vinyl halides or analogous substrates with a nucleophile, *i.e.* the choice between the Ad_N-E and S_N2-Vin mechanism, have not been clearly assessed.

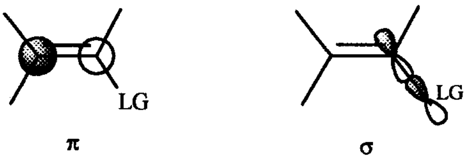
The comparison of the reaction modalities to thiirenium ions[13] (occurring with configurational inversion) and to thiirene dioxide[31] (with retention) led to the suggestion[14,29] that the S_N2-Vin mechanism would require the synergic action of charged super leaving group and of the ring strain relief.

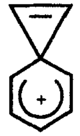
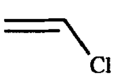
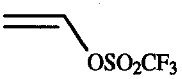
However, a more general and deeper understanding might be obtained by the analysis of the nodal properties of the attacked vacant orbitals at the vinyl carbon.[32] This assumption implies that the direction of the approaching nucleophile is mainly governed by the two-electron interaction between the HOMO of the nucleophile and the LUMO (or the more affected vacant orbital) of the electrophile, with a less determining contribution from the four π electron HOMO-HOMO interaction.

To this aim we performed *ab-initio* computations[33] (at the 6-31G*//3-21G* level) on a series of model vinyl substrates with substituents of different nucleofugalities. In Tables II we give the orbital energies of the first vacant orbitals with π or σ local symmetry at the vinyl carbons. Thus we implicitly assume that the nucleophile approach is determined by the directional properties of the lowest attacked orbital. Within this assumption, we privilege considerations based on the orbital energy gap, rather than those based on orbital overlap.

TABLE II

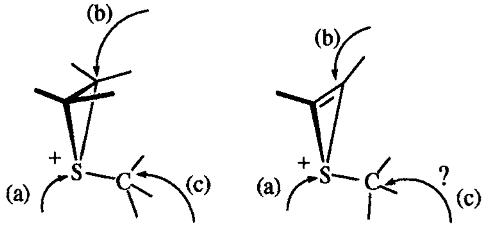
Energies (hartree, 6-31G*//3-21G* level) of the lowest occupied orbitals (LUMO and LUMO+1 = NLUMO) with π and σ symmetry for a series of model electrophiles.



		LUMO (symmetry)	**LUMO+1** (symmetry)
10		-0.0991 (σ)	-0.0865 (π)
11		0.0953 (π)	0.1908 (σ)
12		-0.1335 (σ)	-0.0601 (π)
13		0.1611 (π)	0.2078 (σ)
14		0.1483 (π)	0.1987 (σ)

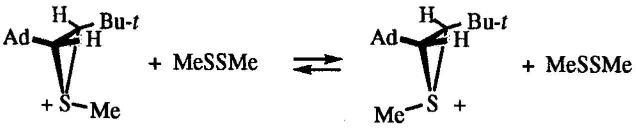
Entries **10** to **13** in Table II are revealing: the models with lowest vacant orbital of local π or σ symmetry at the vinyl system correspond to actual molecules which undergo nucleophilic substitution with retention or inversion respectively. The solvolysis of vinyl triflates occurs with predominant inversion of configuration while the orbital ordering in entry **14** would suggest the Ad$_N$-E mechanism; as matter of fact the solvolysis of these substrates was explained with a non concerted dissociation to a vinyl cation intermediate.[34] Alternatively, it may be suggested that vinyl substrates with a good leaving group (such as vinyl triflates) may undergo a precocious bond stretching (also with some contribution by the solvent), generating a species similar to a vinyl cation, with a LUMO of σ symmetry, and subjected to in-plane nucleophilic attack ("loose" S_N2 mechanism).[35]

Direct Studies. The availability of thiiranium and thiirenium ions as relatively stable species, as well as the results of the theoretical studies, led us to start an investigation on the reactions of nucleophiles on these cations. The potential electrophilic centers are the sulfonium sulfur, the ring carbons and the exocyclic substituent at sulfur. The aim was to obtain direct information on the relative reactivity at sulfonium sulfur and at ring carbons as a function of the substitution pattern and the intrinsic properties of the nucleophile. Path c has been observed only in one limiting case, for thiiranium ions,[36] and can be at all dismissed for thiirenium ions, where the leaving group would be the very unstable thiirene.



SCHEME 8

Preliminary experiments indicated that the reactions with many nucleophiles, among them disulfides, methanol, chloride ion,[37] are rather fast and complex. Thus we begun with a very simple reaction: the nucleophilic attack at sulfonium sulfur by dimethyldisulfide which catalyzes the reversible isomerization of *t*-2-adamantyl-*c*-3-*tert*-butyl-*S*-methylthiiranium hexachloroantimonate **15** into the *trans*- isomer **16**.



15 **16**

SCHEME 9

The nucleophilic attack at sulfur on thiiranium and thiirenium ions, which are generated in only one form, can be studied with a disulfide which brings about a substitution at the sulfonium sulfur: this allowed the extension of the study to a few other thiiranium and thiirenium ions with dialkyldisulfide always in dichloromethane at 25 °C.

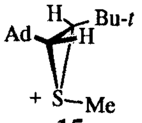
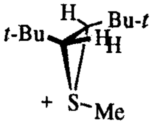
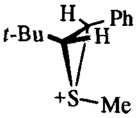
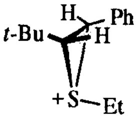
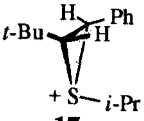
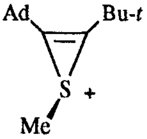
SCHEME 10

The secon order rate constants for forward and reverse reaction, as well the rate constants for other side reactions, have been obtained from the integrated NMR signals through Runge-Kutta numerical integration[38] and Simplex optimization.[39] The substrates, the reaction conditions and the rate constants are reported in Table III.

A few comments are in order on these results: i) if it is assumed that the reactivity of sulfonium sulfur with nucleophiles is about the same for compounds **5** and **15**, the rate difference for the isomerization of **15** by dimethyl disulfide and the *S*-methyl/*S*-ethyl substitution of **5** has to be attributed to the different nucleophilicities of the two disulfides (a factor of about 2). If we apply this correction to the rate of *S*-methyl/*S*-ethyl substitution of **17a**, the virtual *S*-methyl/*S*-ethyl substitution rate of this substrate would be halved. It follows that the relative rates for **17c**:**17b**:**17a** are 1:23:35. These numbers should be associated with the relative stabilities of thiiranium ions and are therefore indicative of the effect of the increasing size of the alkyl substituent at sulfur. The trend is correct but the magnitude is somewhat larger than expected. ii) the greater reactivity of *tert*-butylphenylthiiranium ion **17** with respect to that of the di-*tert*-butyl analogue **5** confirms the stabilizing effect of thiiranium ions by alkyl substituents compared to that by aryl substituents. iii) thiirenium ion **18** is more reactive than similarly substituted thiiranium ion **15** by a factor of about 100. That is not unexpected because the unsaturated three membered rings have higer strain energy than the saturated counterpart. This is know for the pair cyclopropane/cyclopropene (26.2 Kcal/mol)[40] and we have calculated that the rearrangement from thiirenium to thietium ion is more exothermic than the corresponding rearrangement of thiiranium to thietanium ion by 9.5 kcal/mol.[41] It must be recalled that the rearrangement rates of thiiranium and thiirenium ions **5** and **4** show the opposite, which again suggest the important role of steric factors in these reactions. iv) the results above reported indicate a very large preference of the studied substrates for the attack at sulfur with respect to attack at carbon. How much that is due to the electrophile and how much to the reagent is not yet possible to assess.

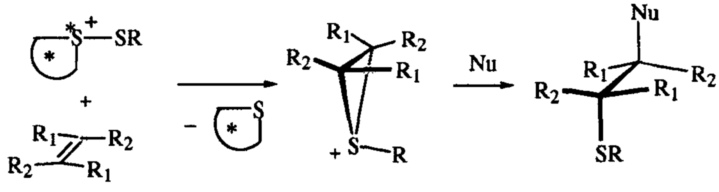
TABLE III

Rate constants for the reactions of thiiranium and thiirenium ions with disulfides in deuterated methylene chloride at 25 °C.

Substrate	Nucleophile	[Nu]/[Sub.]	k_1 ($M^{-1}s^{-1}$)	Rel. Rates	
 **15**	MeSSMe	125	2.09×10^{-5}	-	0.5
 **5**	EtSSEt	37	4.5×10^{-5}	-	1
 **17a**	EtSSEt	6	4.42×10^{-3}	35 (70)	100
 **17b**	MeSSMe	6.5	1.38×10^{-3}	23	-
 **17c**	MeSSMe	25	5.92×10^{-5}	1	-
 **18**	EtSSEt	2	4.39×10^{-3}	-	100

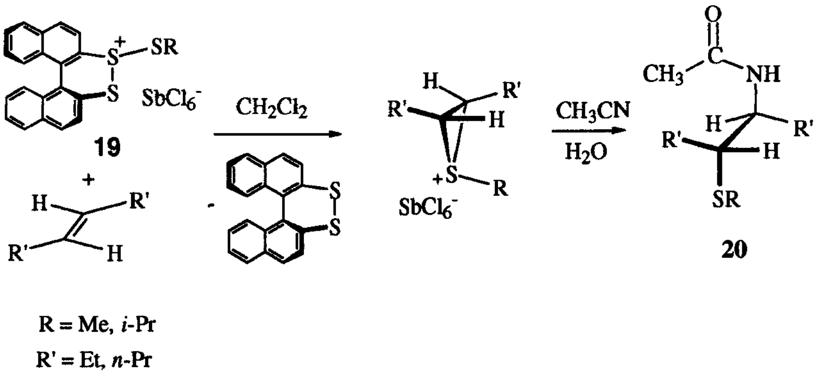
Chiral non racemic thiiranium ions as intermediates in enantioselective synthesis. The relative stability of thiiranium ions suggested us to open a new route to the doubly enantioselective functionalization of the C-C double bond *via* the synthesis of optically active thiiranium ions and the subsequent ring opening by an appropriate nucleophile.

The chiral thiiranium ion was obtained by the transfer of R-S^+ ion from a chiral non racemic sulfonium salt to a pro-chiral unfunctionalized alkene (see Scheme 11).[42]



SCHEME 11

The chiral auxiliary which has given so far the best results is the dinaphto[2,1-*c*:1',2'-*e*][1,2]dithiine[43] which by reaction in dichloromethane with methanesulfenyl chloride and antimony pentachloride affords the sulfonium salt **19** (Scheme 12), isolated and characterized by NMR. The solution of **19** in dry methylene chloride cooled at the selected temperature was allowed to react with *trans*-3-hexene in slightly more than equimolar concentration (see Table IV for details). The solution was then reacted with acetonitrile as nucleophile and then with water to give the final adduct **20** (see Scheme 12). A selection of the results obtained are presented in Table IV.



SCHEME 12

TABLE IV

Enantioselective transfer of CH_3S^+ to *trans*-3-hexene from the enantiopure *S*-methyl hexachloroantimonate salt **19**.

run	Olefin equivalents	t (°C)	time before CH_3CN addition (min)	Product, e.e.(%)[a]
1	1.1	-20	10	40[b]
2	1.1	-20	10	49[b]
3	1.1	-60	60	56[c]
4	1.0	-78	120	86[c]

a. determined on the isolated product *via* ^{1}H NMR utilising (+)-*S*- or (-)-*R*-1-(9-anthryl)-2,2,2-trifluoroethanol. *b.* The chemical yields on product and on recovered disulfide are about 80%. *c.* A by product containing the MeS-S-binaphtho-S- residue is formed in about 30% yield.

The enantiomeric excesses obtained are rather interesting and worth of further investigations. We hope that with the help of the general studies, that we are independently pursuing, we may select better conditions, and perhaps better chiral auxiliaries.

The study already done suggests that the very critical point is the ease of the attack by an achiral nucleophile to the thiiranium ion to give an alternative achiral S-methyl transfer agent which would necessarily give racemic thiiranium ion and racemic final product.

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