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X-ray Structures and Anionotropic Rearrangements of Di-*tert*-butyl-Substituted Thiiranium and Thiirenium Ions. A Structure−Reactivity Relationship

Riccardo Destro,[*,†] Vittorio Lucchini,[*,‡] Giorgio Modena,[§] and Lucia Pasquato[*,§]

Dipartimento di Chimica Fisica ed Elettrochimica and Centro CNR CSRSRC, Università di Milano, via Golgi 19, 20133 Milano, Italy, Dipartimento di Scienze Ambientali, Università di Venezia, Dorsoduro 2137, 30123 Venezia, Italy, and Centro CNR Meccanismi di Reazioni Organiche and Dipartimento di Chimica Organica, Università di Padova, via Marzolo 1, 35131 Padova, Italy

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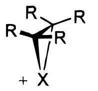
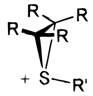
The X-ray structures of *c*-2,*t*-3-di-*tert*-butyl-*r*-1-methylthiiranium **8** BF_4^-, *t*-2,*t*-3-di-*tert*-butyl-*r*-1-methylthiiranium ion **10** BF_4^-, and 2,3-di-*tert*-butyl-1-methylthiirenium **11** BF_4^- have been determined. The $\Delta G^{\ddagger}_{298}$ values for the rearrangements from the cis and the trans *tert*-butyl groups of **8** $SbCl_6^-$ to thietanium ion (two intramolecular S_N2 displacements) and for the rearrangement of **11** $SbCl_6^-$ to thietium ion (an intramolecular S_N2-Vin displacement) are linearly correlated with the strengths of the C−S breaking bonds, suggesting that the two mechanisms are, in the absence of steric hindrance, uniquely governed by the nucleofugality of the sulfonium leaving group.

Haloiranium ions **1** and thiiranium ions **2**, the intermediates of the electrophilic addition of halogens and of sulfenyl halides to alkenes, can be easily detected by spectroscopic methods.[1] However, only iranium ions with bulky substituents at the ring carbons, which are capable of hindering the approach of nucleophiles, are stable enough to be isolated as crystals that, in some case, have been analyzed by X-ray diffraction. The necessity of a heavy substitution pattern is particularly stringent in the case of haloiranium ions: only the ions persubstituted at ring carbons with bulky groups, as the halonium ions **3** of adamantylideneadamantane,[2] could be studied by diffractometric analysis. On the other hand, besides that of the sulfonium ion **4** of adamantylideneadamantane,[3] X-ray structures are available of thiiranium ions with only two bulky substituents at ring carbons, as in the case of the sulfonium ion **5** of 1,2-dimethylacenaphthylene.[4]



1: X = Br, I



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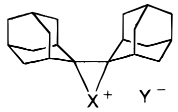
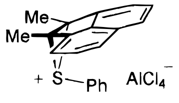


3a: X = Cl, Y = $SbCl_6$
3b: X = Br, Y = Br_3, SO_3CF_3
3c: X = I, Y = SO_3CF_3
4: X = SPh, Y = SO_3CF_3



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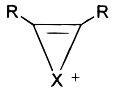
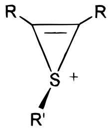


6: X = Cl, Br, I



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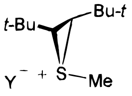
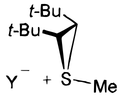
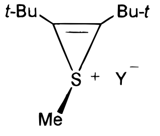


8a: Y = $SbCl_6$
8b: Y = BF_4



10a: Y = $SbCl_6$
10b: Y = BF_4



11a: Y = $SbCl_6$
11b: Y = BF_4
11c: Y = PF_6

This dichotomy is more pronounced in the case of haloirenium ions **6** and thiirenium ions **7**, the intermediates of the electrophilic addition to alkynes. Haloirenium ions have never been detected, while thiirenium ions, also when lacking bulky substituents at ring carbons, have been spectroscopically detected at low temperature.[5] With bulky substituents, as *tert*-butyl groups, thiirenium ions could be isolated and examined by X-ray diffraction.[6] It has been argued that the lower stability of haloirenium ions may derive from the destabilizing four electron-two orbital interaction between the C−C π system and the heteroatom lone pair.[7] This interaction is minimized in thiirenium ions by the pyramidal arrangement around sulfur, which pushes the lone pair away from the C−C π system.

We have described the rearrangement of *c*-2,*t*-3-di-*tert*-butyl-*r*-1-methylthiiranium ion **8** hexachloroantimonate into thietanium ion **9** (Scheme 1).[8] The methyl migration from the cis *tert*-butyl group is noticeably faster than that

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[†] CSRSRC-CNR, University of Milano.

[‡] University of Venezia.

[§] CMRO-CNR, University of Padova.

(1) First detection of haloiranium ions: Olah, G. A.; Bollinger, J. M.; Brinich, J. *J. Am. Chem. Soc.* **1968**, *90*, 2587. First detection of thiiranium ions: Goodman, L.; Benitez, A.; Baker, B. R. *J. Am. Chem. Soc.* **1958**, *80*, 1680.

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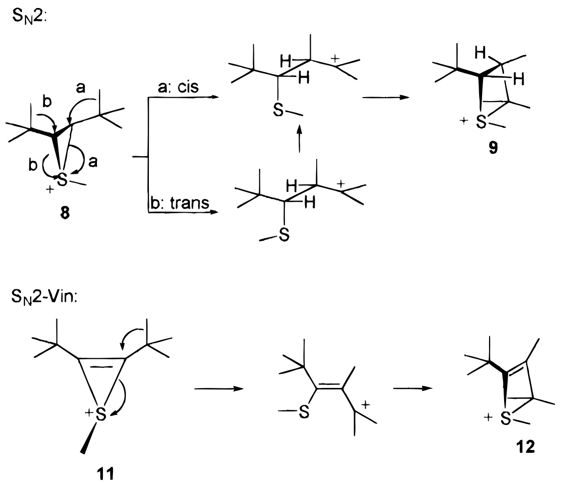
Scheme 1



from the trans *tert*-butyl group. The potential rearrangement of *t*-2,*t*-3-di-*tert*-butyl-*r*-1-methylthiiranium ion **10** hexachloroantimonate is obscured by competing faster reactions.[8,9]

More recently, we have also described the rearrangement of 2,3-di-*tert*-butyl-1-methylthiirenium **11** hexachloroantimonate into thietium ion **12** (Scheme 1).[10] The rearrangement occurs with the slowest rate. The rearrangement rates for **8** and **11** in CD_2Cl_2 at 25 °C are reported in Table 1, together with the corresponding activation free energies.

The rearrangements of the thiiranium ion **8** are intramolecular nucleophilic displacements at an aliphatic carbon occurring with the ubiquitous S_N2 mechanism, that of thiirenium ion **11** is a displacement at a vinyl carbon occurring with the seldom observed S_N2-Vin in-plane mechanism.[10,11] In the vast majority of cases, the nucleophilic substitution at the vinyl carbon occurs with the Ad_N-E out-of-plane mechanism.[12] The steric hindrance exerted by the substituents at the vinyl carbon to the in-plane approaching of the external nucleophile has been invoked[13] as the main factor that favors the Ad_N-E rather than the S_N2-Vin mechanism. The presence of this steric effect makes impossible a meaningful comparison of the S_N2 and S_N2-Vin mechanisms. This hindrance is completely eliminated in the rearrangements described in Scheme 1, where the nucleophilic methyl group approaches the electrophilic sp^3 or sp^2 ring carbon virtually unhindered.

To find an alternative rational for the reactivity ordering detailed in Table 1, we have undertaken an X-ray investigation of thiiranium ions **8** and **10** and of thiirenium ions **11**. We have performed the analysis on species with different counteranions: hexachloroantimonate **10a**, tetrafluoroborates **8b**, **10b**, and **11b**, and hexafluorophosphate **11c**.

Results and Discussion

X-ray Structures. The crystal data for compounds **8b**, **10a**, **10b**, **11b**, and **11c** are given in the Supporting Information.[15]

The main features of the experimental molecular geometries obtained by X-ray analysis of **8b**, **10b**, and **11b** are reported in Table 2. Molecular conformations and numbering schemes for the corresponding thiiranium and thiirenium ions are shown in the ORTEP plots[16] of Figure 1.

An exhaustive discussion of the molecular geometry is given in the Supporting Information. In this section, we will discuss only those features that are relevant for the structure–reactivity relationship.

Differences in geometry between the thiiranium ions of **8b** and **10b** are clearly dictated by steric reasons: the relief from hindrance between the two *tert*-butyl groups of **10b** is achieved by (i) stretching the C2–C3 bond by 0.048 Å, as compared to the same bond in **8b**, and (ii) increasing the C2–C3–C5 and C3–C2–C4 bond angles by about 10°, as compared to the corresponding angles in **8b**. Deformations in the thiiranium ion of **8b** are also related to interactions of the methyl group at sulfur with the nearest methyl of the *tert*-butyl group at C2 (see Figure 1). Here, we note that (i) the S–C2–C4 angle is enlarged by more than 8° with respect to the S–C3–C5 angle; (ii) the C2–S bond is longer than the C3–S bond by 0.016 Å; (iii) the C1 methyl group is pushed away from the plane perpendicular to the ring plane, containing the S atom and bisecting the C2–C3 bond. This arrangement of the C1 methyl group is reflected in the difference by about 6° between the two exocyclic bond angles at the sulfur atom: C2–S–C1, 112.6°, and C3–S–C1, 106.8°. As a result of these deformations, the shortest intramolecular distances between atoms of the two C1 and C6 methyl groups are only marginally shorter than the sum of van der Waals radii: C1···C6, 3.29(1) Å; H1B···H6B, 2.34(7) Å; and H1C···H6B, 2.37(7) Å. The presence in **8b** of a ring S–C2 bond slightly, yet significantly, longer than the S–C3 bond is worthy of note: it is the single geometrical feature that may be related to the different rearrangement rates for methyl migration from cis and trans *tert*-butyl groups in trans thiiranium ions **8** (see Table 1). This point will be treated in more details in the following section.

Some relevant features of the thiirenium ion in **11b** are as follows: (i) the length of the C2–C3 ring bond, 1.278 Å, even shorter than the C–C double bond in cyclopropene, 1.294 Å;[17] (ii) the lengths of the endocyclic S–C bonds, shorter by about 0.03 Å (even if overestimated corrections are considered) than those of the thiiranium ions in **8b** and **10b**; (iii) the lengths of the C2–C4 and C3–C5 bonds <1.50 Å, shorter by 0.02–0.03 Å than those of the thiiranium ions in **8b** and **10b**. All

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(15) Atomic coordinates, displacement parameters and full listings of bond lengths and angles for **8b**, **10b**, and **11b** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as deposition nos. CCDC-117659, -117658, and -117660, respectively. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Table 1. Kinetic Constants and Activation Energies at 25 °C for the Rearrangement of Ions 8a and 11a Compared with Selected Geometrical Features of Ions 8b and 11b

rearrangement	k_{298}, s^{-1}	$\Delta G^{\ddagger}_{298}$, kcal mol^{-1}	bond lengths,[a] Å	torsion angles, deg
8: cis	7.42×10^{-6} [b]	24.4	C2−S: 1.876	S−C2−C4−C8: −174.3
8: trans	3.83×10^{-7} [b]	26.2	C3−S: 1.860	S−C3−C5−C7: −163.5
11	6.30×10^{-8} [c]	27.3	C2−S: 1.831	S−C2−C4−C6: −168.3

[a] Corrected for thermal motion. [b] Reference 8. [c] Reference 10.

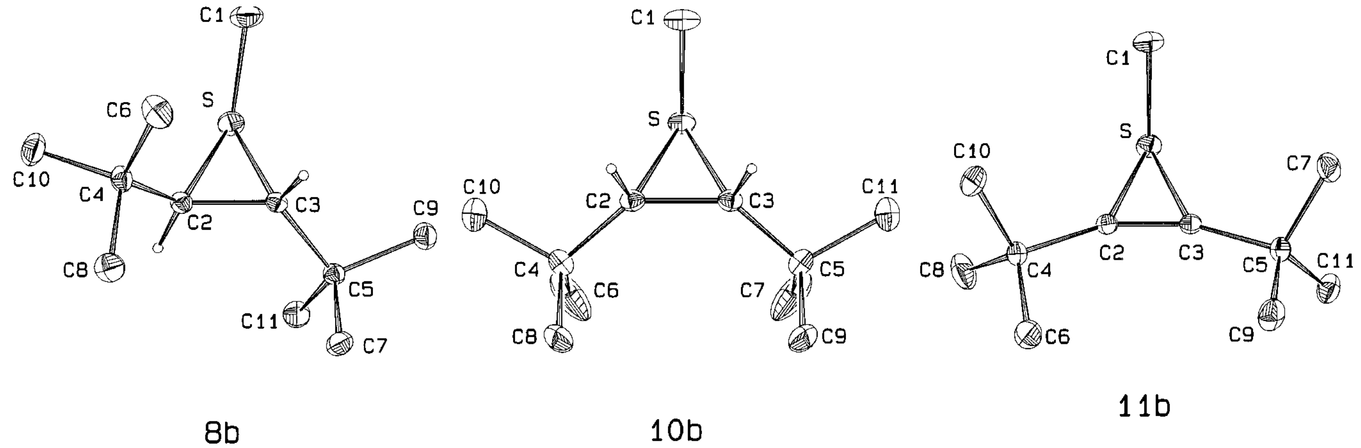

Figure 1. ORTEP plots of the thiiranium ion of **8b**, the thiiranium ion of **10b**, and the thiirenium ion of **11b**, with atom numbering scheme. For the sake of clarity, only the H ring atoms of thiiranium ions are reported, as spheres of arbitrary radius. Because of the *m* crystallographic symmetry, in **10b** the odd-labeled C atoms C3 to C11 are mirror images of the even-labeled C atoms C2 to C10.

Table 2. Some Relevant Bond Lengths[a] (Å) and Angles (Deg) for 8b, 10b, and 11b, Obtained by X-ray Analysis[b]

	8b	**10b**	**11b**
C1−S	1.809(8)	1.807(4)	1.817(2)
C2−S	1.876(4)	1.859(3)	1.831(1)
C3−S	1.860(4)	1.859(3)	1.831(2)
C2−C3	1.452(6)	1.500(6)	1.278(3)
C2−C4	1.518(5)	1.531(4)	1.497(3)
C3−C5	1.527(6)	1.531(4)	1.496(3)
C2−S−C3	45.7(1)	47.6(2)	40.85(9)
S−C2−C3	66.6(2)	66.21(9)	69.5(1)
S−C3−C2	67.7(2)	66.21(9)	69.6(1)
S−C2−C4	125.1(2)	119.2(2)	134.0(1)
S−C3−C5	117.1(3)	119.2(2)	133.3(1)
C3−C2−C4	127.0(3)	135.4(2)	156.4(2)
C2−C3−C5	125.5(3)	135.4(2)	157.1(1)

[a] Corrected for thermal motion effects after **TLS** analysis (ref 14). [b] Standard uncertainties in parentheses.

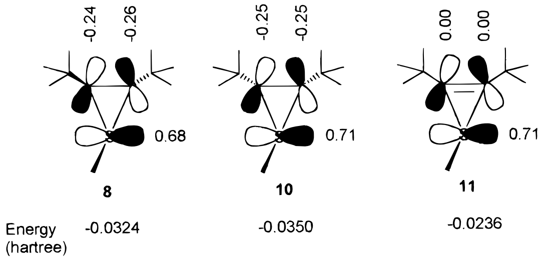

Figure 2. Natural atomic charges and shapes and energies (hartree) of the LUMOs of thiiranium ions **8** and **10** and of thiirenium ion **11**.[18]

these features are consistent with the sp^2 nature of the ring C atoms.

Rearrangement Rates and Geometrical Features of Thiiranium Ion 8 and Thiirenium Ion 11. The rearrangements illustrated in Scheme 1 can be now discussed in light of the structural data reported above. These processes will occur virtually unhindered by substituents at the electrophilic ring carbon, but with the modality required for intramolecular nucleophilic displacements, i.e., the antiperiplanarity between the migrating methyl and the sulfur leaving group.

Indeed, this may be the rational that would explain why the rearrangement has not been observed in the case of thiiranium ion **10**: it may be argued that the reciprocal steric hindrance will compel the two *tert*-butyl groups to orientations presenting no methyl antiperiplanar to the C−S bond.

The data reported in Table 1 show that this requirement is equally obeyed for the cis and the trans S_N2 rearrangements of thiiranium ion **8** as well as for the S_N2-Vin rearrangement of thiirenium ion **11**. The torsion angles S−C2−C4−C8 and S−C3−C5−C7 in **8b** and S−C2−C4−C6 (or S−C3−C5−C9) in **11b** are all close to 180°. The antiperiplanarity cannot constitute a differentiating factor.

Inspection of structure **10b** in Figure 1 reveals that thiiranium ion **10** also presents methyl groups that are almost antiperiplanar to the C−S bond. We can therefore confirm the earlier hypothesis[8,9] that the rearrangement is also possible in this ion, but it is hindered by faster competing reactions.

A second differentiating element may be the electrophilicity of the ring carbons, as measured by the charge at these atoms and by the shape and energy of the LUMOs. The geometries of ions **8**, **10**, and **11** have been optimized ab initio with Spartan 4.0 program package[18] at the 3-21G* level. Natural atomic charges and orbital energies have been calculated at the same level. These parameters, together with the orbital shapes, are illustrated in Figure 2. The full computational results will be reported elsewhere.[19]

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(18) Spartan 4.0 program pakage, 1995, distributed by Wavefunction, Inc., Irvive, CA 92715.

(19) Destro, R.; Lucchini, V.; Modena, G.; Pasquato, L. Manuscript in preparation.

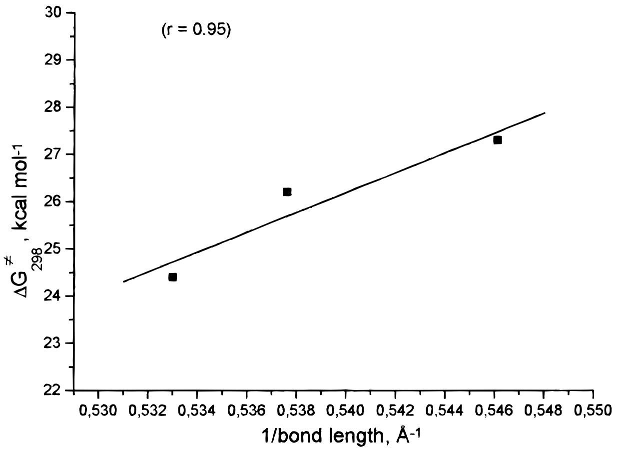

Figure 3. Correlation between the $\Delta G^{\ddagger}_{298}$ (kcal mol^{-1})values for the rearrangements in Scheme 1 and the strengths of the breaking C−S bonds (measured as the reciprocals of the bond lengths, Å^{-1}).

The LUMOs of thiiranium ions **8** and **10** and of thiirenium ion **11** have the same Walsh-type shape, so that the overlaps with the orbital of the migrating methyl should be similar. The LUMO energy is slightly higher in the case of thiirenium ion **11** then in the case of thiiranium ions **8** and **10**: the greater energy gap with relevant occupied orbital of the migrating methyl will disfavor the interaction. On the other hand, the more positive natural atomic charge at the ring carbons of thiirenium ion **11** will favor methyl migration. Natural charges and LUMO energies should compensate each other with the result that electrophilicity is a non differentiating factor.

We are left with the nucleofugality of the sulfur atom as measured by the lengths of the bonds between this atom and the electrophilic ring carbon. We have already pointed out in the previous section the reasons that determine the order of endocyclic C−S bond lengths in ions **8b** and **11b**.

The correlation of the activation free energies is more correctly made with the strength of the breaking bond, and therefore with the reciprocal of the bond length (which has the same dimension of a wavenumber). An acceptable linear correlation ($r = 0.953$) between these two parameters is found (Figure 3). Although the magnitude of the set (only three elements) is rather limited, we would propose that, in the absence of steric hindrance, the S_N2 mechanism in thiiranium ions and the S_N2-Vin mechanisms in thiirenium ions are determined by the same factor, the nucleofugality of the leaving group.

The correlation shown in Figure 3 has been validated by ab initio investigation of the rearrangements shown in Scheme 1 and also of the not yet observed rearrangement of thiiranium ion **10**.[19]

Conclusions

What makes the in-plane approach of the nucleophile and the S_N2-Vin mechanism so seldom observed in intermolecular nucleophilic displacements at the vinyl carbon is the availability of an alternative path: the out-of-plane approach occurring with the Ad_N-E mechanism.[12] The shift toward this mechanism is favored by two factors. (i) In the vast majority of cases, the LUMO of the electrophile is the π^* orbital, which overlaps best with the occupied orbital of the nucleophile when this latter approaches out-of-plane. In some rare systems (as the thiirenium ions) the LUMO is an in-plane σ^* orbital, and actually, in most of these cases the nucleophile approaches in-plane.[11] (ii) The in-plane substituents at the vinyl system may present a relevant steric hindrance to the in-plane approach of the nucleophile, but surely to a smaller extent to the out-of-plane approach.

We would propose that, in the absence of steric effects affecting the nucleophilic displacement at the vinyl carbon, the S_N2 and S_N2-Vin mechanism are, also in the intermolecular displacement by an external nucleophile, equally governed by the nucleofugality of the leaving group.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded at 200 or 250 MHz, ^{13}C NMR spectra at 62.9 MHz, using CD_2Cl_2 or liquid SO_2 as solvent. Commercial reagents and known compounds were 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. The syntheses and spectroscopic data of compounds **8a**,[8] **8b**,[9] **10a**,[8] **10b**,[9] **11a**,[20] and **11b**[20] have been already reported.

2,3-Di-*tert*-butyl-1-methylthiirenium Hexafluorophosphate (11c). In a 25 mL three-neck flask containing methylbis(methylthio)sulfonium hexafluorophosphate[21] (0.195 g, 0.68 mmol), SO_2 was condensed to 10 mL at −78 °C under nitrogen atmosphere and 3,3,5,5-tetramethyl-4-hexyne[22] (0.096 g, 0.70 mmol), dissolved in 1 mL of dry CH_2Cl_2, was added in one portion. The reaction mixture was left at −78 °C for 40 min, and then, after addition of 5 mL of dry CH_2Cl_2, SO_2 was allowed to evaporate. The salt was precipitated with pentane and recrystallized from CH_2Cl_2/pentane at −20 °C with 60% yield. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.50 (9H, s, *t*-Bu), 2.60 (3H, s, Me). ^{13}C NMR (62.9 MHz, CD_2Cl_2) δ: 27.64, 29.59, 33.38, 114.52.

X-ray Diffraction Studies. Crystals suitable for X-ray analysis were grown from saturated solutions of the salts in CH_2Cl_2 at −20 °C. Alternatively, pentane was added to the mixture up to the point it became turbid, and then the solution was left undisturbed at −20 °C until formation of the crystals.

Supporting Information Available: Crystallographic data for compounds **8b**, **10b**, and **11b** together with structure refinement, crystal data for compounds **10a** and **11c**, and comparison of these X-ray structures with those previously reported for thiiranium ions **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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