The complete and irreversible conversion of a *cis* carbon-substituted thiiranium ion into the *trans* isomer

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***t*-2-*tert*-Butyl-*t*-3-phenyl-*r*-1-methylthiiranium 1 isomerizes into the more stable (32.3 kJ mol^{-1}) *t*-2-*tert*-butyl-*c*-3-phenyl-*r*-1-methylthiiranium 2 in a complete and irreversible process (monitored by proton NMR at −30 °C) *via* an open benzylic carbenium ion.**

Thiiranium ions, the bridged intermediates in the addition of sulfenyl derivatives to alkenes,[1,2] are known to be among the most stable of the iranium ion family with respect to the isomeric open carbonium ions.[1,2] Isolation of these cyclic species[3] and their characterization in the solid state by X-ray structural determination[4–6] and in solution mainly by NMR spectroscopy[7,8] together with theoretical *ab initio* calculations[6,9] have provided detailed information on their structure.

Thiiranium ions are responsible for the complete *anti* stereospecificity of the additions of sulfenyl halides to alkenes. Few exceptions are known† and they concern, mainly, those alkenes having electron-donor substituents. For example, in the sulfenylation of vinyl ethers the thiiranium ion may be in equilibrium with the open carbonium ion stabilized *via* the mesomeric oxonium ion.[12]

Recently, we began to investigate the chemistry of stable and isolated thiiranium ions for mechanistic[8,13,14] as well as for synthetic reasons.[15] Bulky substituents at the ring carbons stabilize the ions, whereas phenyl substituents activate the α-carbon toward nucleophilic reactions. Here we report that we could observe, for the first time, the unexpected complete isomerization of the *t*-2-*tert*-butyl-*t*-3-phenyl-*r*-1-methylthiiranium **1** hexachloroantimonate into the *t*-2-*tert*-butyl-*c*-3-phenyl-*r*-1-methylthiiranium **2** hexachloroantimonate.

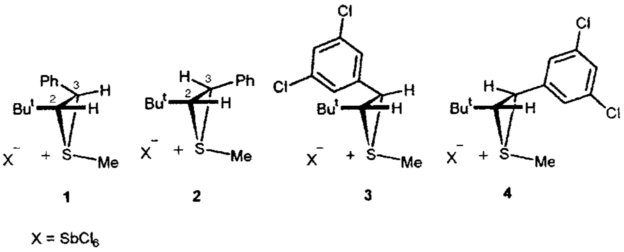
The *t*-2-*tert*-butyl-*c*-3-phenyl-*r*-1-methylthiiranium **2** hexachloroantimonate was prepared by reaction of (*E*)-3,3-dimethyl-1-phenylbut-1-ene with 1 equiv. of methylthio(bismethylthio)sulfonium hexachloroantimonate in CH_2Cl_2 at −20 °C.[14] Only the isomer having the phenyl ring *cis* to the *S*-methyl group is formed.[14] When we attempted the synthesis of the *t*-2-*tert*-butyl-*t*-3-phenyl-*r*-1-methylthiiranium **1** hexachloroantimonate by adding the same electrophile to the (*Z*)-3,3-dimethyl-1-phenylbut-1-ene at −20 °C, only the *trans* isomer **2** was obtained. The reaction repeated in CD_2Cl_2 and monitored by ^{1}H-NMR at −20 °C confirmed the exclusive formation of the *trans* thiiranium ion **2**.

However, the addition of CH_3SCl in CH_2Cl_2 at −78 °C to (*E*)- and (*Z*)-3,3-dimethyl-1-phenylbut-1-ene is completely stereoselective and hence the corresponding thiiranium ions must be the intermediates.

Indeed, when the reaction of the (*Z*)-alkene with $Me_3S_3SbCl_6$ was carried out at −50 °C in an NMR tube we could observe the slow formation of the *cis* thiiranium ion **1**.‡ The reaction is complete in about 30 min. Very diagnostic are the doublets relative to protons 2-H and 3-H which in the *trans* isomer are at 4.38 and 5.56 ppm respectively (*J* 12.0 Hz) whereas in the *cis* isomer 2-H and 3-H are doublets at 4.52 and 5.65 ppm (*J* 10.14 Hz). Also, the *S*-methyl group shows a singlet at 2.95 ppm in the *cis* isomer and at 2.16 ppm in the *trans* isomer.

Raising the temperature gradually up to −30 °C we observed the quantitative isomerization of the *cis* isomer **1** into the *trans* one ($t_{1/2}$ is about 2 h) without detecting any significant amount of (*Z*)-alkene suggesting that the isomerization occurs on the thiiranium ion itself, likely *via* a ring opening–ring closure process as depicted in Scheme 1.§

To confirm the hypothesis of Scheme 1, *i.e.* that the observed isomerization is due to an equilibrium between thiiranium ion and the corresponding carbonium ion, we prepared the *t*-2-*tert*-butyl-*t*-3-(3,5-dichlorophenyl)-*r*-1-methylthiiranium **3** hexachloroantimonate and the *t*-2-*tert*-butyl-*c*-3-(3,5-dichlorophenyl)-*r*-1-methylthiiranium **4** hexachloroantimonate, where the phenyl group is substituted by the more electronegative 3,5-dichlorophenyl residue, by addition of methylthio(bismethylthio)sulfonium hexachloroantimonate to (*Z*)- and (*E*)-1-(3,5-dichlorophenyl)-3,3-dimethylbut-1-enes¶ in CH_2Cl_2 at −60 °C.

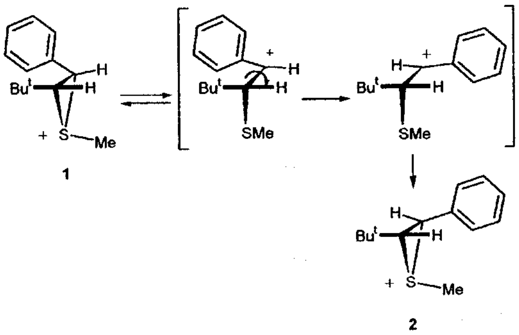


Scheme 1

As expected thiiranium ion **3** is much more stable than the homologous **1** in CD_2Cl_2. At 0 °C the compound is stable for more than 12 h.||

Independent information on the relative stability of thiiranium ions **1** and **2** has been obtained by *ab initio* calculation.** Optimization at the RHF/3-21G*//RHF-3-21G* level gives an energy difference of 32.3 kJ mol^{-1} between the most stable *trans* and the *cis* isomer. The stronger steric interaction between the phenyl ring and the *cis tert*-butyl group in the ion **1** with respect to the steric interaction between the phenyl ring and the *S*-methyl group in the *trans* ion **2** may be responsible for the calculated energy difference.

In the optimized geometry relative to the *trans* thiiranium ion **2** the S–C(3) bond is 1.991 Å whereas the S–C(2) bond is 1.870 Å. The same bonds in the *cis* ion **1** are 1.855 and 1.884 Å respectively. The C(2)–C(3) bonds in the two isomers **1** and **2**



Scheme 2

are similar being 1.463 and 1.488 Å respectively. Very likely the *cis* interaction between the phenyl and the S–Me group in the ion **2** is minimized by stretching the S–C(3) bond. The much greater steric interaction between the *tert*-butyl and the *cis* phenyl moieties in the *cis* ion **1** is removed very efficiently by breaking the S–C(3) bond due to the presence of the phenyl ring which stabilizes the α positive charge in the open carbonium ion. Rotation around the C(2)–C(3) bond and closure to the *trans* ion **2** complete the rearrangement process (Scheme 1). The energy difference between the two ions ensures an irreversible reaction.

In conclusion, we have reported the isomerization of the *t*-2-*tert*-butyl-*t*-3-phenyl-*r*-1-methylthiiranium ion **1** to the more stable *trans* isomer **2** *via* an open benzylic carbonium ion. The different stability of these ions (32.3 kJ mol^{-1}) makes the process irreversible. Efforts are in progress in our laboratories to find suitable thiiranium ions to study the different reactivity modes of *cis* carbon-substituted thiiranium ions with respect to *trans* ones.

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Notes and references

† It has been reported that sulfenyl halides add stereospecifically to (*E*)- and (*Z*)-but-2-ene in the temperature range −34 to +146 °C (ref. 10). The corresponding thiiranium ions may be independently synthesized and they react with nucleophiles at −20 °C to give the non-isomerized adducts. However, a mixture of *erythro* and *threo* products, whose composition is independent of the starting thiiranium ion, is formed if the thiiranium ion salts are kept for some time at +20 °C (ref. 11).

‡ δ_H(CD_2Cl_2, 200 MHz, −50 °C) 0.92 (9H, s, Bu^t); 2.95 (3H, s, Me), 4.52 (1H, d, *J* 10.14), 5.65 (1H, d, *J* 10.14), 7.45 (5H, m, Ph). δ_C(CD_2Cl_2, 62.9 MHz, −50 °C) 23.46, 27.31, 33.88, 63.96, 75.02, 124.91, 127.42, 128.55, 129.14.

§ The stability of the (*Z*)-alkene was independently checked in CD_2Cl_2 in the range −30 to +25 °C by ^1H NMR.

¶ Both isomers were obtained from the corresponding alkyne prepared following the procedure reported in ref. 16. The (*Z*)-isomer was then obtained by hydroboration with catecholborane (ref. 17); the (*E*)-alkene was prepared by photochemical isomerization of the (*Z*)-isomer.

|| The rather large difference in reactivity observed between *cis* thiiranium ions **1** and **3** is not unexpected since the reaction may be compared to a carbonium ion formation process from a neutral substrate. The difference in sigma values for phenyl and 3,5-dichlorophenyl is 2 × 0.37 which applied to a unimolecular process having rho values of −4 leads to an estimate value for the reactivity ratio of 10^{-3}.

** Spartan 5.0 program package, distributed by Wavefunction, Inc., Irvine, CA 92715.

1 G. Capozzi, G. Modena and L. Pasquato, *The Chemistry of Sulphenyl Halides and Sulphenamides*, ed. S. Patai, Wiley, Chichester, 1990, p. 403.
2 V. Lucchini, G. Modena and L. Pasquato, *Gazz. Chim. Ital.*, 1997, **127**, 177.
3 D. J. Pettit and G. K. Helmkamp, *J. Org. Chem.*, 1963, **28**, 2932.
4 G. I. Borodkin, Y. V. Gatilov, E. I. Chernyak and V. G. Shubin, *Izv. Akad. Nauk SSSR, Ser. Kim.*, 1985, 2826 (*Chem. Abstr.*, 1986, **105**, 208686); G. I. Borodkin, Y. V. Gatilov, E. I. Chernyak and V. G. Shubin, *Izv. Akad. Nauk SSSR, Ser. Kim.*, 1987, 2230 (*Chem. Abstr.*, 1987, **108**, 186453).
5 X. Huang, R. J. Batchelor, F. W. Einstein and A. J. Bennet, *J. Org. Chem.*, 1994, **59**, 7108.
6 L. Pasquato, R. Destro, V. Lucchini and G. Modena, *Phosphorus Sulfur Silicon Relat. Elem.*, in the press.
7 G. Capozzi, O. De Lucchi, V. Lucchini and G. Modena, *Tetrahedron Lett.*, 1975, 2603.
8 V. Lucchini, G. Modena and L. Pasquato, *J. Am. Chem. Soc.*, 1988, **110**, 6900; V. Lucchini, G. Modena and L. Pasquato, *J. Am. Chem. Soc.*, 1991, **113**, 6600.
9 Y. Kikuzono, T. Yamabe, S. Nagata, H. Kato and K. Fukui, *Tetrahedron*, 1974, **30**, 2197; J. W. Gordon, G. H. Schmid and I. G. Csizmadia, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1722.
10 G. H. Schmid and V. M. Csizmadia, *Can. J. Chem.*, 1966, **44**, 1338.
11 W. A. Smit, M. Z. Krimer and E. A. Vorobieva, *Tetrahedron Lett.*, 1975, 2451; E. A. Vorobieva, M. Z. Krimer and W. A. Smit, *Izv. Akad. Nauk SSSR, Ser. Kim.*, 1976, 2743.
12 For example: K. C. Nicolaou, T. Ladduwahetty, J. L. Randall and A. Chucholowski, *J. Am. Chem. Soc.*, 1986, **108**, 2466; T. Sato, J. Otera and H. Nozaki, *J. Org. Chem.*, 1990, **55**, 6116; K. Kudo, Y. Hashimoto, M. Sukegawa, M. Hasegawa and K. Saigo, *J. Org. Chem.*, 1993, **58**, 579; D. K. Jones and D. C. Liotta, *Tetrahedron Lett.*, 1993, **34**, 7209; D. K. Jones and D. C. Liotta, *Adv. Mol. Model.*, 1995, **3**, 67.
13 V. Lucchini, G. Modena, M. Pasi and L. Pasquato, *J. Org. Chem.*, 1997, **62**, 7018.
14 M. Fachini, V. Lucchini, G. Modena, M. Pasi and L. Pasquato, *J. Am. Chem. Soc.*, 1999, **121**, 3944.
15 V. Lucchini, G. Modena and L. Pasquato, *J. Chem. Soc., Chem. Commun.*, 1994, 1565.
16 Z.-Y. Yang and D. J. Burton, *Tetrahedron Lett.*, 1990, **31**, 1369.
17 H. C. Brown and S. K. Gupta, *J. Am. Chem. Soc.*, 1972, **94**, 4370.

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