A Novel Reaction of Thiirane Cation Radicals in Solution: the Formation of 5,6-Diphenyl-1,2,3,4-tetrathianes through Trisulphurated Thiirane Cation Radical Intermediates

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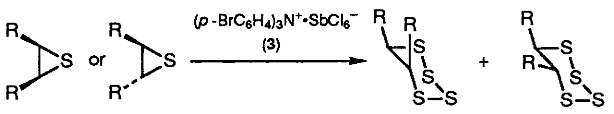
A novel reaction of thiirane cation radicals to form *cis*- and *trans*-5,6-diphenyl-1,2,3,4-tetrathianes [*cis*-(**2**) and *trans*-(**2**)] took place when *cis*- and *trans*-2,3-diphenylthiiranes [*cis*-(**1**) and *trans*-(**1**)] were mixed with a catalytic amount of tris(*p*-bromophenyl)aminium hexachloroantimonate (**3**) in dichloromethane.

Williams and co-workers recently demonstrated,[1] on the basis of γ-ray irradiation-ESR studies in Freon matrices, that the thiirane hemi-bonded dimer cation radical[2] formed from the initially generated thiirane cation radical undergoes ethylene extrusion, giving the sulphurated thiirane cation radical. Interestingly, in mass spectroscopic studies,[3] subsequent two-fold sulphur-transfer propagations to give the trisulphurated thiirane cation radical were observed. However, neither mechanistic details of the ethylene extrusion nor the fate of trisulphurated cation radicals could be explored under those single electron-transfer (SET) conditions. In solution-phase SET reactions,[4] on the other hand, no similar reaction of the thiirane cation radical has been observed. Herein we report a novel reaction of thiirane cation radicals; a mixture of *cis*- and *trans*-5,6-diphenyl-1,2,3,4-tetrathianes [*cis*-(**2**) and *trans*-(**2**)] was obtained *via* tris(*p*-bromophenyl)aminium hexachloroantimonate (**3**)-catalysed SET reactions of *cis*- and *trans*-2,3-diphenylthiiranes [*cis*-(**1**) and *trans*-(**1**)] in dichloromethane.



cis-(**1**) *trans*-(**1**) *cis*-(**2**) *trans*-(**2**)

Scheme 1. R = Ph.

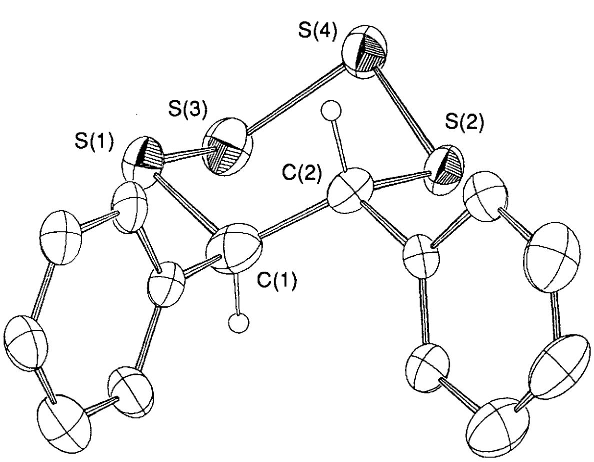
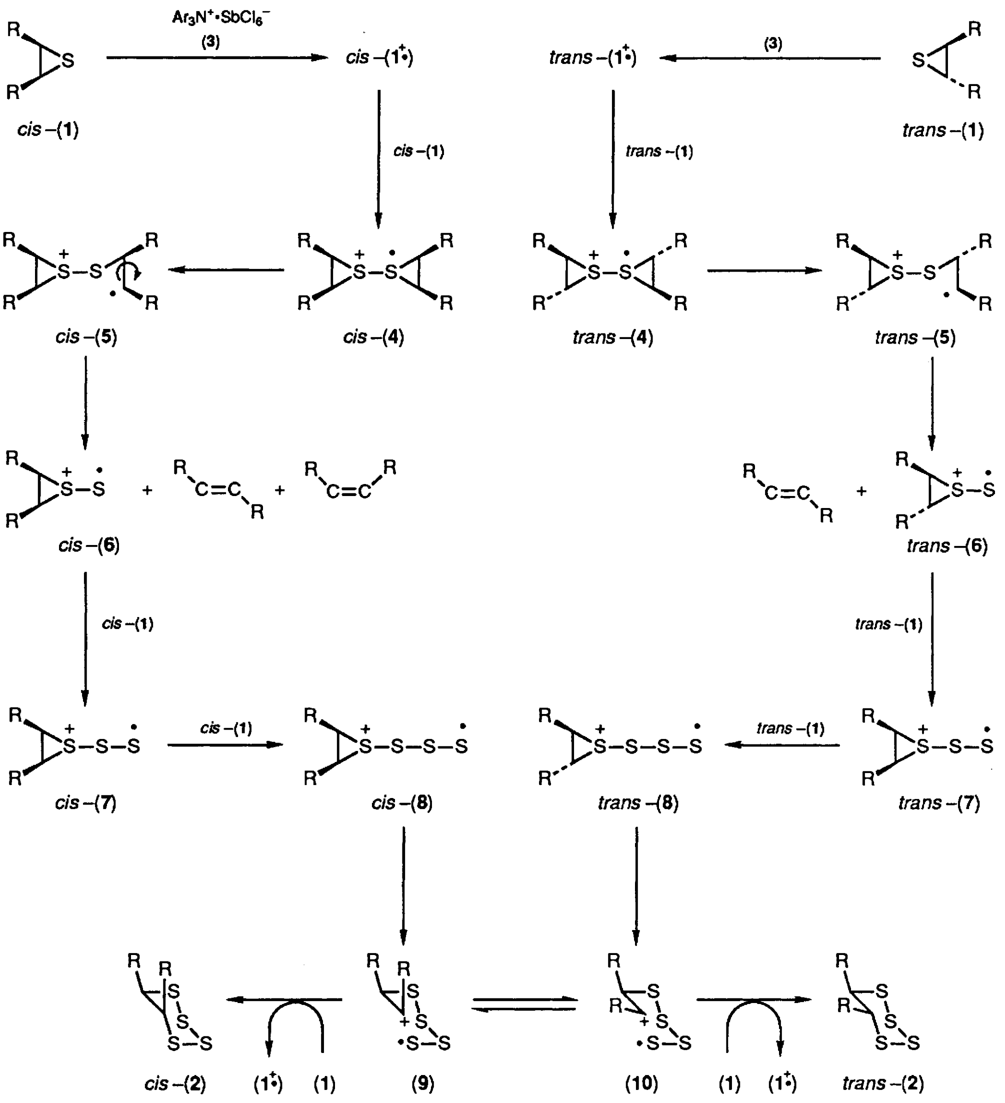


Figure 1. ORTEP drawing of *trans*-(**2**).



Scheme 2. Ar = p-BrC$_6$H$_4$, R = Ph.

A typical experimental procedure is as follows. Aminium radical salt (**3**) (0.10 mmol)[5] was added to a stirred solution of *cis*-(**1**) (1.00 mmol)† in nitrogen-saturated dry dichloromethane (20 ml) and the mixture was stirred for 1 h at 0 °C. Quenching of the reaction with 1,4-diazabicyclo[2.2.2]octane followed by chromatographic separation afforded *cis*-(**2**) (5%)‡ and *trans*-(**2**) (12%)‡ together with *cis*-stilbene (30%), *trans*-stilbene (38%), and sulphur (6%). Similarly, *trans*-(**1**)† afforded a mixture of *cis*-(**2**) (2%), *trans*-(**2**) (7%), *trans*-stilbene (68%), and sulphur (9%), but *cis*-stilbene was not obtained at all. The structure of *trans*-(**2**) was determined by *X*-ray crystallographic analysis; the molecule showed *trans* configuration of two phenyl groups with a chair conformation for the six-membered ring (Figure 1).§ The structure of *cis*-(**2**)

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† Compounds *cis*-(**1**) and *trans*-(**1**) were prepared by the literature method.[6] E_p^{ox}[*cis*-(**1**)] 1.64 V, E_p^{ox}[*trans*-(**1**)] 1.57 V *vs.* standard calomel electrode (SCE) in acetonitrile.

‡ If our proposed mechanism in Scheme 2 is valid, the maximum yield of tetrathiane (**2**) relative to starting thiirane (**1**) should be no higher than 25%. Satisfactory elemental analyses were obtained for *cis*- and *trans*-(**2**). *Selected data* for *cis*-(**2**): oil; ^{1}H NMR (90 MHz, CDCl$_3$) δ 5.03 (s, 2H), 7.12 (br. s, 10H). For *trans*-(**2**): m.p. 145.5—146 °C; ^{1}H NMR (90 MHz, CDCl$_3$) δ 4.86 (s, 2H), 7.14 (br. s, 10H). E_p^{ox} [*trans*-(**2**)] 1.98 V *vs.* SCE in acetonitrile.

§ *Crystal data* for *trans*-(**2**): C$_{14}$H$_{12}$S$_4$, M = 308.51, monoclinic, space group *Cc*, a = 14.842(1), b = 14.524(1), c = 27.978(2) Å, β = 104.41(1)°, U = 5841.5(7) Å^3, Z = 16, D_c = 1.403 g cm^{-3}. A colourless plate-like crystal, 0.2 × 0.15 × 0.1 mm^3 was used for the data collection on a Rigaku automated four-circle diffractometer (AFC-5R) with rotating anode. A total of 3667 independent reflections was collected using graphite monochromated Cu-K_α radiation within 2θ = 110°. The structure was solved by direct methods using the RANTAN 81 program with some modification and non-standard inputs, and the parameters for S and C atoms were refined by the block-diagonal least-squares method with anisotropic temperature factors. Some hydrogen atoms were located in the difference Fourier map, and were included in the refinement (isotropic temperature factors) with others calculated geometrically. The final R value is 0.063 for 2725 reflections with $|F_o| > 3\sigma|F_o|$. No absorption correction was applied. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

was confirmed by the comparison of its ^{1}H NMR spectrum with that of *trans*-(**2**).¶

Detailed mechanistic studies further provided the following results. (i) Addition of 1,2,4,5-tetramethoxybenzene|| (10 equiv.) to (**3**), which is known to be an effective SET quencher,[8] suppressed the formation of tetrathianes, while anisole|| (10 equiv.) did not. (ii) Varying the amount of (**3**) (0.10—0.50 equiv.) to *cis*- and *trans*-(**1**) did not significantly change the yields of tetrathianes. (iii) Addition of sulphur (S_8) did not change the yields of tetrathianes. (iv) Treatment of *cis*-stilbene with (**3**) in dichloromethane at 0 °C for 1 h gave a mixture of 83% of *cis*-stilbene and 5% of *trans*-stilbene, whereas no isomerization occurred in the reaction of *trans*-stilbene. Taking the above observations into account, a plausible mechanism is proposed in Scheme 2.

The initially formed *cis*-($\mathbf{1}^{\cdot+}$) reacts with *cis*-(**1**) to form the thiirane dimer cation radical *cis*-(**4**). The C–S bond cleavage of *cis*-(**4**) gives *cis*-(**5**) which, by the rotation around the C–C bond and subsequent C–S bond fission, is converted to *cis*-(**6**) and a 1 : 1 mixture of *cis*- and *trans*-stilbenes. Similar two-fold sulphur-transfer propagations successively take place to give *cis*-(**7**) and -(**8**) and the *cis*- and *trans*-stilbenes. On the other hand, *trans*-(**1**), by similar sequential three-fold sulphur-transfer propagations, gives *trans*-(**8**) together with *trans*-stilbene. These sequential three-fold sulphur-transfer propagation steps are as expected from matrix isolation[1] and mass spectroscopic studies.[3] However, the ethylene extrusion apparently occurs in a stepwise rather than a concerted manner. Formal 1,4-sigmatropic rearrangements of *cis*-(**8**) and *trans*-(**8**) to give a mixture of *cis*-(**2**) and *trans*-(**2**) similarly proceed *via* a stepwise cleavage–cyclization mechanism through an equilibrium mixture of (**9**) and (**10**). The back electron-transfer from (**1**) to cis-($\mathbf{2}^{\cdot+}$) and *trans*-($\mathbf{2}^{\cdot+}$), regenerates ($\mathbf{1}^{\cdot+}$) which enters into a chain cycle.[4b]

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¶ There have been several examples of tetrathiane preparations;[7] however the formation of tetrathianes through cation radical intermediates has never been observed.

|| Oxidation potentials (E_p^ox) of tetramethoxybenzene and anisole are 0.77 and 1.77 V *vs.* SCE, respectively, in acetonitrile.