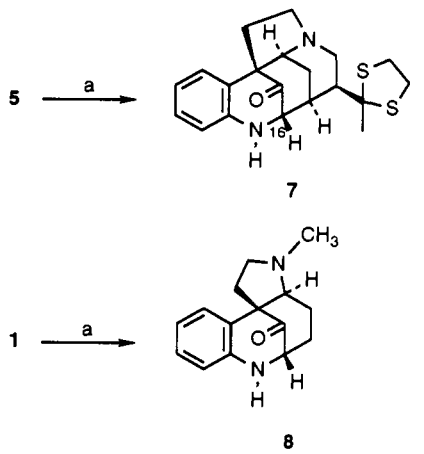
Scheme II[a]



[a] (a) $CH(NMe_2)_3$ (5 equiv), THF, reflux, 5 h.

4 was converted into dithioacetal **5** (80%), which was then treated with Bu_3SnH to give the alkaloid tubifolidine (50%)[9] in a single step involving desulfurization and simultaneous closure of the indoline ring by reduction of the α-(*o*-nitrophenyl) ketone moiety.[10]

Methoxycarbonylation of the key azatricyclic intermediate **5** rendered the corresponding β-keto ester (50%), with recovery of all the unreacted starting material. Deprotection of the C-19 carbonyl group (85%) followed by catalytic hydrogenation in the presence of 1 equiv of acid[11] furnished the pentacyclic compound **6** (75%). Finally, $NaBH_4$ reduction of the acetyl side chain took place diastereoselectively to give the alkaloid echitamidine (80%). The ^1H NMR and ^{13}C NMR spectra of synthetic (±)-echitamidine were identical with those reported for the natural product.[5c,12]

Surprisingly, attempts to introduce a formyl substituent at C-16 in compound **5** using $CH(NMe_2)_3$[13] in THF led to the pentacyclic tetrahydroquinoline **7** (72%) (Scheme II). This unprecedented reductive cyclization implies that the amidinium cation generated by loss of a dimethylamide anion from $CH(NMe_2)_3$ acts as a reducing instead of a formylating agent (tetramethylurea was isolated)[14] to give an intermediate nitroso derivative.[15] Intramolecular nucleophilic attack of the enolate at C-16 to the nitroso group, followed by further reduction, would lead to **7**. The scope of this new reaction seems to be quite general as, under the same reaction conditions, nitro ketone **1** provided (92%) the bridged tetrahydroquinoline **8**.[16]

Acknowledgment. This work was supported by the DGICYT (Projects PB88-0316 and PB91-0800).

Supplementary Material Available: NMR spectra of the synthesized compounds and HRMS of compounds **7** and **8** (29 pages). Ordering information is given on any current masthead page.

(9) This synthetic compound was identical with tubifolidine previously synthesized by a different procedure.[1a]

(10) In contrast, aliphatic nitro groups suffer a reductive cleavage by Bu_3SnH. For a review, see: Ono, N.; Kaji, A. *Synthesis* **1986**, 693.

(11) Hydrogenation under basic (Li_2CO_3) or neutral conditions afforded the corresponding carbinolamine, whereas in the presence of an excess of acid partial epimerization at C-20 was observed.

(12) Oguakwa, J. U.; Galeffi, C.; Messana, I.; Patamia, M.; Nicoletti, M.; Marini-Bettolo, G.-B. *Gazz. Chim. Ital.* **1983**, *113*, 533.

(13) For a review of the chemistry of tris(dimethylamino)methane and related formamide acetals, see: Abdulla, R. F.; Brinkmeyer, R. S. *Tetrahedron* **1979**, *35*, 1675.

(14) We thank a reviewer for this suggestion and Prof. Julio Delgado (University of La Laguna) for helpful discussion regarding the structures of **7** and **8**.

(15) For a related reduction of a nitro group, see: Dickinson, W. B. *J. Am. Chem. Soc.* **1964**, *86*, 3580.

(16) For the NMR analysis of aspernomine, a fungal metabolite with a similar bridged tetrahydroquinoline moiety, see: Staub, G. M.; Gloer, J. B.; Wicklow, D. T.; Dowd, P. F. *J. Am. Chem. Soc.* **1992**, *114*, 1015.

The First Stable Stannanethione in Solution Derived from a Kinetically Stabilized Diarylstannylene

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The chemistry of double-bond compounds between group 14 metals and heavier chalcogen atoms has continued to occupy the attention of chemists in various fields. Although there have been some examples of silanethione,[1] silaneselone,[1] and germanethiones[2] stabilized by taking advantage of electronic stabilization, stannanethiones, i.e., a tin analogue of thioketones, such as $t\text{-}Bu_2Sn{=}S$ and $Ph_2Sn{=}S$ are known only as transient species, undergoing ready oligomerization to give the corresponding dimer and trimer, respectively.[3,4] We report herein the synthesis of diarylstannanethione Tb(Tip)Sn=S (**1a**, Tip = 2,4,6-triisopropylphenyl), the first stable stannanethione in solution at room temperature, via kinetically stabilized diarylstannylene Tb(Tip)Sn: (**2a**) by taking advantage of an excellent steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tb hereafter),[5] which was developed in the course of our study on the sterically congested molecules.

Stannylene **2a** was readily obtained by the treatment of a THF solution of TbLi with an ether suspension of stannous chloride (1.0 equiv) at −78 °C for 2 h followed by the addition of a THF solution of an equimolar amount of TipLi at the same temperature.[6] Under inert atmosphere, stannylene **2a** was found to be quite stable even at 60 °C, and it showed a deep purple color (λ_{max} = 561 nm) after the solvent exchange into hexane. ^{119}Sn NMR spectra of **2a** in toluene-d_8 showed only one signal at 2208 ppm, attributable to the chemical shift of a divalent organotin compound.[7] The formation of **2a**, which was also confirmed by the trapping experiments using 2,3-dimethyl-1,3-butadiene and benzil giving the expected [1 + 4] adducts **3**[6] and **4**[6] (37 and 22%) as shown in Scheme I, is of great interest since it represents a monomeric diarylstannylene stable without any intramolecular coordination by heteroatoms.[8] The remarkable stability of this sterically protected stannylene **2a** prompted us to examine its sulfurization, which is expected to lead to the formation of stable stannanethione **1a**.

(1) Arya, P.; Boyer, J.; Carrē, F.; Corriu, R.; Lanneau, G.; Lapasset, J.; Perrot, M.; Priou, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1016.

(2) (a) Veith, M.; Becker, S.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1237. (b) Veith, M.; Detemple, A.; Huch, H. *Chem. Ber.* **1991**, *124*, 1135.

(3) Puff, H.; Gattermayer, R.; Hundt, R.; Zimmer, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 547.

(4) Schumann, H. *Z. Anorg. Allg. Chem.* **1967**, *354*, 192.

(5) (a) Okazaki, R.; Unno, M.; Inamoto, N. *Chem. Lett.* **1987**, 2293. (b) Okazaki, R.; Unno, M.; Inamoto, N.; Yamamoto, G. *Ibid.* **1989**, 493. (c) Okazaki, R.; Unno, M.; Inamoto, N. *Ibid.* **1989**, 791.

(6) Experimental details for the formation of **1a**, **2a**, and **7** and the physical properties of **3–9** are described in the supplementary material.

(7) The bandwidth and the chemical shift of **2a** were almost unchanged between −30 and 60 °C in toluene-d_8, indicating the absence of a monomer–dimer equilibrium in this temperature range. Recently, Kira et al. reported the synthesis of a stable, monomeric dialkylstannylene, 2,2,5,5-tetrakis(trimethylsilyl)-1-stannacyclopentane-1,1-diyl, the ^{119}Sn NMR spectrum of which showed a sharp singlet at 2323 ppm without any temperature dependence: Kira, M.; Yauchibara, R.; Hirano, R.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 7785. Bis[bis(trimethylsilyl)methyl]stannylene has been reported to show δ_{Sn} at 2315 (toluene-d_8, 375 K): Zilm, K. W.; Lawless, G. A.; Merrill, R. M.; Millar, J. M.; Webb, G. G. *J. Am. Chem. Soc.* **1987**, *109*, 7236. See also Cotton, J. D.; Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2275.

(8) For bis[2,4,6-tris(trifluoromethyl)phenyl]stannylene, a diarylstannylene stabilized by the intramolecular coordination of fluorine atoms toward the tin atom, see Grützmacher, H.; Pritzkow, H.; Edelmann, F. T. *Organometallics* **1991**, *10*, 23.

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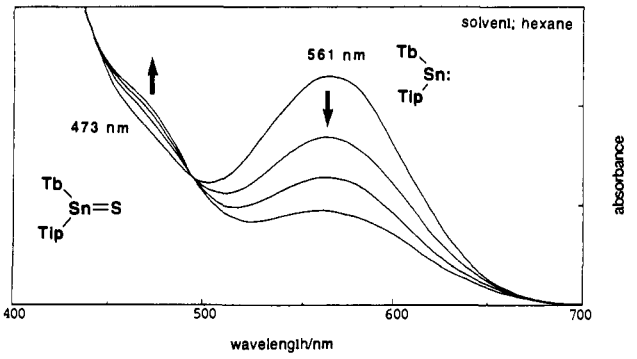
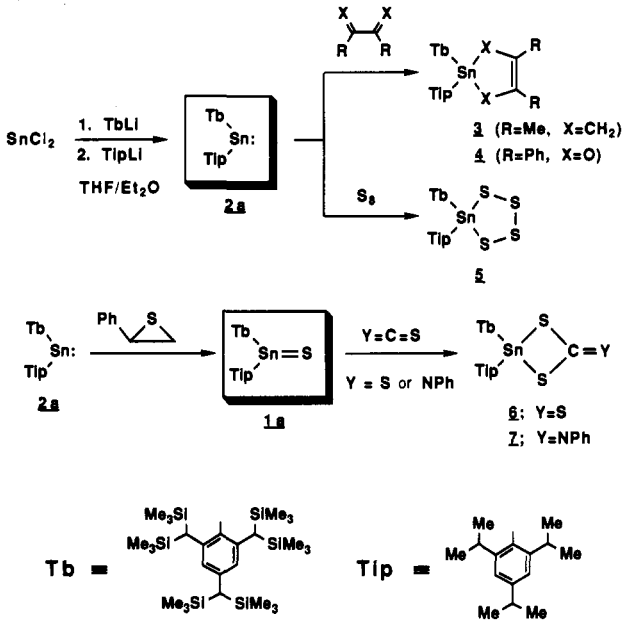


Figure 1. UV-vis spectral change in the reaction of Tb(Tip)Sn: (**2a**) with styrene episulfide in hexane.

Scheme I



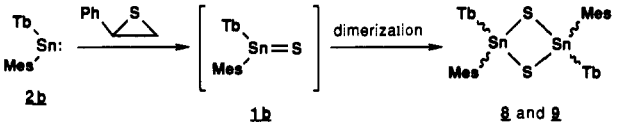
In contrast to the successful formation of germanium-sulfur double-bond compounds by the reactions of thermodynamically stabilized germylene with elemental sulfur,[2] only 1,2,3,4,5-tetrathiastannolane **5**[6,9] was isolated (9%) as a sulfurized product upon treatment of stannylene **2a** with elemental sulfur (Scheme I). On the other hand, when the deep purple solution of **2a** in hexane was treated with styrene episulfide at room temperature, the solution turned yellow, suggesting the formation of stannanethione **1a**.[6] Monitoring of the reaction using UV-vis spectroscopy showed an appearance of a new absorption at 473 nm (shoulder) at the expense of the absorption of stannylene **2a** at 561 nm, as shown in Figure 1, the absorption of 473 nm being assignable to the n-π^* transition of the tin-sulfur double bond of stannanethione **1a**.

Furthermore, the formation of stannanethione **1a** was chemically evidenced by the fact that treatment of the yellow solution thus obtained with an excess amount of thiocumulenes such as carbon disulfide and phenyl isothiocyanate at room temperature afforded 1,3,2-dithiastannetane derivatives **6**[6,10] and **7**[6] in 19 and 38% yields, respectively. The formation of adducts **6** and **7** is worthy of note from the standpoint of the first examples of [2 + 2] cycloaddition of a tin-sulfur double-bond compound except for self-dimerization.[11]

(9) For similar 1,2,3,4,5-tetrathiametallolanes of group 14 metals, see Tokitoh, N.; Suzuki, H.; Matsumoto, T.; Matsuhashi, Y.; Okazaki, R.; Goto, M. *J. Am. Chem. Soc.* **1991**, *113*, 7047.

(10) The structures of **6**, **8**, and **9** were firmly established by X-ray crystallographic analysis, whose details will be described in a full paper in the near future.

Scheme II



Since the reaction of less hindered diarylstannylene Tb(Mes)Sn: (**2b**; Mes = mesityl) with styrene episulfide in THF at -78 °C gave no monomeric products but a mixture of cis and trans isomers of 1,3,2,4-dithiadistannetanes **8** and **9** (total 11%, cis/trans = ca. 1:1)[6,10] (Scheme II), which are the dimerization products of the intermediary stannanethione Tb(Mes)Sn=S (**1b**), the prominent stability of the stannanethione **1a** is obviously due to the steric demand of the combination of Tb and Tip groups.

Further investigation on the reactivity of the novel stannanethione is currently in progress.

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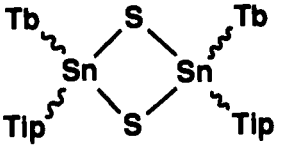
Supplementary Material Available: Experimental details for the formation of **1a**, **2a**, and **7**, and spectral and analytical data of **3**-**9** (5 pages). Ordering information is given on any current masthead page.

(11) The possibility that a chemical species involved in these cycloadditions is a dimer instead of a monomer (**1a**) or a monomer dissociated to a minor extent from a dimer can be eliminated by the fact that both *cis*- and *trans*-dithiadistannetanes **10**, the dimers of **1a**, are totally inert to the thiocumulenes under the reaction conditions (i.e., room temperature). Although **1a** is stable at room temperature, it undergoes dimerization, giving **10** (*cis*-**10** 2%, *trans*-**10** 6%) at 90 °C in the absence of a tapping reagent.



10

Practical, High-Yield, Regioselective, Rhodium-Catalyzed Hydroformylation of Functionalized α-Olefins

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Hydroformylation has been an industrially important process for several decades.[2] In general, the harsh reaction conditions required and/or the lack of selectivity observed has limited the utility of hydroformylation in the preparation of functionalized organic molecules.[3] The report in 1988 of a catalytic system which

(1) National Science Foundation Predoctoral Fellow 1989-1992.

(2) (a) Claus, R. E.; Schreiber, S. L. *Org. Synth.* **1986**, *64*, 150 and references therein. (b) Webster, F. X.; Rivas-Enterrios, J.; Silverstein, R. M. *J. Org. Chem.* **1987**, *52*, 689. (c) Ogawa, H.; Chihara, T.; Taya, K. *J. Am. Chem. Soc.* **1985**, *107*, 1365.

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