A New Method for the Synthesis of Stannylenes: Exhaustive Desulfurization of Tetrathiastannolanes

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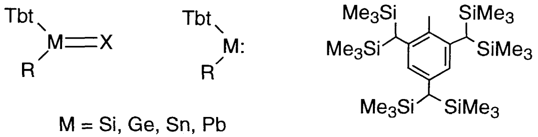
Exhaustive desulfurization of overcrowded diaryl-substituted 1,2,3,4,5-tetrathiastannolanes having a 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group on the tin atom resulted in the formation of the corresponding kinetically stabilized diarylstannylenes, the formation of which was confirmed by the characteristic electronic absorptions attributable to the n-p transitions of stannylene, and by the chemical trapping by 2,3-dimethyl-1,3-butadiene.

Recently, much attention has been focused on the low-coordinated compounds of heavier group 14 elements (Si, Ge, Sn, and Pb) such as double-bond compounds and divalent species (higher homologues of a carbene). Although the divalent species of silicon and germanium (silylenes and germylenes) have been well studied, the corresponding organotin compounds (stannylenes) have been relatively less explored.[1-4] Until now a few stable stannylenes have been synthesized from stannous chloride and organolithium reagents.[2-4] We have also reported the efficient synthesis of a stable diarylstannylene by the dehalogenation of the corresponding dibromostannane with lithium naphthalenide.[5, 6]

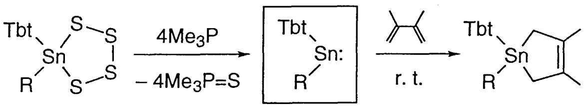


M = Si, Ge, Sn, Pb
X = S, Se

(Tbt)

On the other hand, we previously reported the first synthesis of silanethione,[7] germanethione,[8] germaneselone,[9] stannanethione,[10] and stannaneselone,[10] which were kinetically stabilized by taking advantage of efficient steric protection by 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter), by the reactions of the corresponding overcrowded tetrachalcogenametallolanes with 3 equivalent phosphine reagents. We now present a new method for the synthesis of stable diarylstannylenes by the exhaustive desulfurization of extremely hindered tetrathiastannolanes with 4 equivalent phosphine reagents.

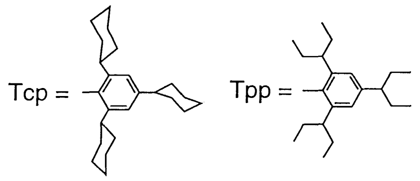
When trimethylphosphine (4 equiv.) was added to a hexane solution of Tbt- and Tcp- (Tcp = 2,4,6-tricyclohexylphenyl) substituted tetrathiastannolane **1a** at room temperature, the reaction mixture turned orange, suggesting the formation of stannanethione, Tbt(Tcp)Sn=S. After stirring for 5 min at room temperature, the solution turned deep blue. The UV-vis spectrum of this solution exhibited an absorption maximum at 586 nm which is assignable to the n–p transition of diarylstannylene, Tbt(Tcp)Sn: (**2a**). The formation of stannylene **2a** was also confirmed by the fact that the treatment of the deep blue solution thus obtained with an excess amount of 2,3-dimethyl-1,3-butadiene afforded the corresponding [4+1]cycloadduct **3a** in 12% yield. On the contrary, the reaction of Tbt- and Tip- (Tip = 2,4,6-triisopropylphenyl) substituted tetrathiagermolane [Tbt(Tip)GeS$_4$] with an excess amount of triphenylphosphine gave hydroxymercaptogermane [Tbt(Tip)Ge(SH)OH].[12] Its formation indicates that the germanethione [Tbt(Tip)Ge=S] did not react with triphenylphosphine but reacted with water during the workup procedure. The easier desulfurization from the stannanethione than that from the germanethione may result from the higher stability of the divalent state for a tin atom and from the lower strength for a tin–sulfur double bond.



1a; R = Tcp
1b; R = Tpp

2

3a; 12%
3b; 18%



Similarly, Tbt- and Tpp- [Tpp = 2,4,6-tris(1-ethylpropyl)-phenyl] substituted tetrathiastannolane **1b** also gave the corresponding stannylene **2b**, which showed an absorption maximum at 563 nm in hexane.[11]

There have been many reports on the chemistry of silirenes (silacyclopropenes), from which silylenes are generated by photolysis or thermolysis.[13] We have recently found that germirenes (germacyclopropenes) having bulky substituents on the germanium atom are also useful precursors for stable germylenes.[14] On the other hand, only one example of stannirene (stannacyclopropene)[15] has been known probably because this type of strained small-ring tin-compounds are thermodynamically unstable and sensitive to air and moisture. For the generation of stannylenes, therefore, only few convenient precursors have been available so far.[1] Although stannylenes are known to be generated by using lithium reagents,[2-6] the existence of impurities such as lithium halides and the basic reaction conditions are their drawback. The present reaction is worthy of note as a novel method for the generation of stannylenes from stable and tractable precursors under neutral conditions although the efficiency of generation of stannylenes **2** from **1**, which was estimated by the yields of the [4+1]cycloadducts **3**, has not been optimized yet because of the dimerization of intermediary stannanethiones during the desulfurization reactions.[16]

As a result of our new findings on the generation of stable stannylenes **2a** and **2b**, we can compare their electronic absorptions with those of the previously reported Tbt-substituted stannylenes **4** and **5**.[3] The most interesting point in the comparison of overcrowded diarylstannylenes which are substituted with one Tbt group and a variety of bulky aromatic substituents, is the effect of a substituent on the n–p transition of stannylenes.

Table 1. Electronic absorptions of stannylenes in hexane at room temperature

Stannylenes	λ_{max}/nm
Tbt(Mes)Sn: **4**	527[a]
Tbt(Tip)Sn: **5**	561[a]
Tbt(Tpp)Sn: **2b**	563
Tbt(Tcp)Sn: **2a**	586

[a] See, Ref 3.

As can be seen in Table 1, the n-p transitions of stannylenes are slightly red-shifted on increasing the bulkiness of the aromatic substituents introduced on the tin atom together with a Tbt group. This red-shift is interpreted most likely in terms of the widening of the C–Sn–C angles as in the case of silylenes[17,18] and germylenes.[19] In other words, the red shifts in these absorption maxima are diagnostic of the degree of steric congestion in these systems; for example, it is concluded that the combination of Tbt and Tcp groups is bulkier than that of Tbt and Tpp groups.

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