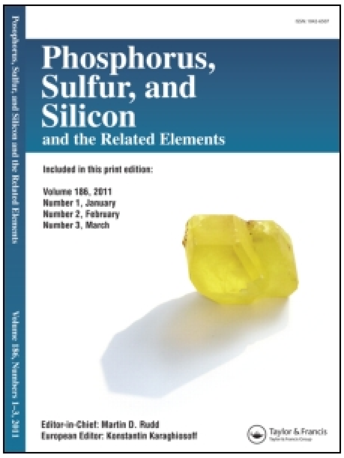

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Synthesis of Tin-Containing Heterocyclic Compounds by the Reaction of 1,3,5,2,4,6-Trichalcogenatristannin with 1,3-Dipoles

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Reaction of 1,3,5,2,4,6-trithiatristannin with 2,4,6-tri-*t*-butylbenzonitrile oxide gave the 1,3,5,2-oxathiazastannole quantitatively. Reaction of 1,3,2,4-dithiadistannetane with 2,4,6-tri-*t*-butylbenzonitrile oxide also quantitatively but slowly afforded the 1,3,5,2-oxathiazastannole. Reaction of 1,3,5,2,4,6-triselenatristannin with 2,4,6-tri-*t*-butylbenzonitrile oxide gave 1,3,5,2-oxaselenazastannole. The thermal behavior of the oxaselenazastannole was unusual.

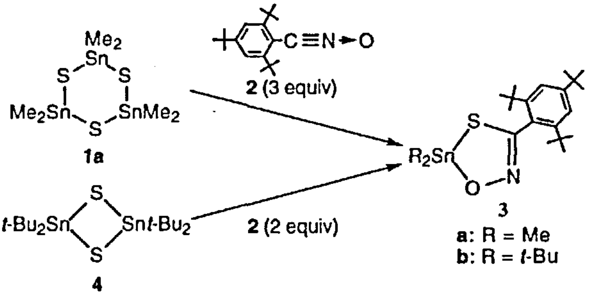
Keywords: 1,3,5,2,4,6-trithiatristannin; 2,4,6-tri-*t*-butylbenzonitrile oxide; 1,3,5,2-oxathiazastannole; 1,3,2,4-dithiadistannetane; 1,3,5,2,4,6-triselenatristannin; 1,3,5,2-oxaselenazastannole

INTRODUCTION

Thermolysis or photolysis of 1,3,5-trichalcogenane derivatives is one of the convenient methods for the generation of double-bond compounds between group 14 and group 16 elements as confirmed by trapping reactions with various reagents.[1] Although such trapping reactions are useful in the synthesis of heterocyclic compounds having group 14 elements, there are few reports on the formation of tin-containing heterocyclic compounds by the reaction of tin analogs of 1,3,5-trichalcogenane with trapping reagents. We now report on the novel reactions of 1,3,5,2,4,6-trichalcogenatristannins with 2,4,6-tri-*t*-butylbenzonitrile oxide to afford the 1,3,5,2-oxachalcogenazastannoles, a new method for the synthesis of organotin heterocycles, and on the unusual thermal dissociation behavior of the resulting 1,3,5,2-oxaselenazastannole. The first X-ray structural analysis of the 1,3,5,2-oxathiazastannole is also reported.

RESULTS AND DISCUSSION

When mesitonitrile oxide (3 equiv) was added to a benzene solution of 1,3,5,2,4,6-trithiatristannin **1a**, a white precipitate was immediately formed, which had a melting point of around 260 °C. Unfortunately, this product was insoluble to most of organic solvents and its structure couldn't be identified. Next we examined the reaction of 2,4,6-tri-*t*-butylbenzonitrile oxide **2**[2] with **1a**. Monitoring the reaction of 1,3,5,2,4,6-trithiatristannin **1a** with nitrile oxide **2** (3 equiv) by ^{1}H NMR in benzene-d_6 at room temperature showed the reaction proceeded cleanly to afford 1,3,5,2-oxathiazastannole **3a**. Although some stable oxachalcogenazastannoles with bulky ligands on the tin were synthesized,[3] **3a** is the first example of the 1,3,5,2-oxachalocogenazastannole having small substituents on the tin. Reaction of 2,2,4,4-tetra-*t*-butyl-1,3,2,4-dithiadistannetane **4**[4] with **2** was also investigated. The reaction proceeded slowly but quantitative formation of 1,3,5,2-oxathiazastannole **3b** was achieved, the structure of which was established by X-ray crystallographic analysis carried out at 203 K (Fig 1). The central five-membered ring was found to have a planar structure.



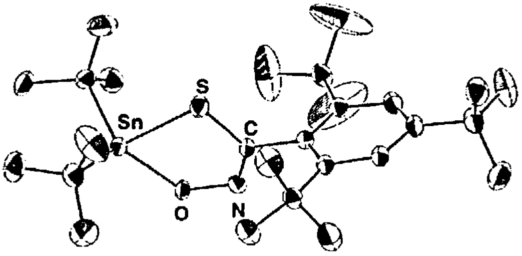
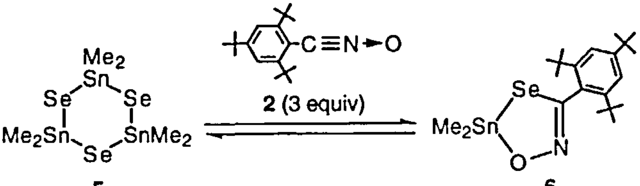


Fig 1. ORTEP drawing of **3b** with thermal ellipsoids plots (40% probability for non-hydrogen atoms).

In contrast to the quantitative formation of **3a** by the reaction of trithiatristannin **1a** with nitrile oxide **2**, the same treatment of 1,3,5,2,4,6-triselenatristannin **5** with **2** (3 equiv) afforded the mixture of 1,3,5,2-oxaselenazastannole **6** and the starting materials. The oxaselenazastannole **6** was isolated as solid sparingly soluble in benzene. Interestingly, when the reaction of **5** and **2** was monitored by ^{1}H NMR in benzene-d_6, the formation of the stannole **6** was observed at room temperature. However, when the solution was heated at 80 °C, the stannole **6** was completely disappeared but formed again after cooling down the solution at room temperature. To our best knowledge, this type of thermal behavior of the oxachalcogenazoles is unprecedented and of interest.



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References

[1] (a) T. Nishio, M. Yoshioka, H. Aoyama, and N. Sugiyama, *Bull. Chem. Soc. Jpn.*, 2253 (1973). (b) H. Lavayssière, J. Satgé, J. Barrau, and M. Traore, *J. Organomet. Chem.*, **240**, 335 (1982). (c) J. Barrau, G. Rima, H. Lavayssière, G. Dousse, and J. Satgé, *J. Organomet. Chem.*, **246**, 227 (1983). (d) P. Boudjouk, S. R. Bahr, and D. P. Thompson, *Organometallics*, **10**, 778 (1991).

[2] T. Matsumoto, N. Tokitoh, and R. Okazaki, private communication.

[3] (a) M. Saito, N. Tokitoh, and R. Okazaki, *J. Organomet. Chem.*, **499**, 43 (1995). (b) M. Saito, N. Tokitoh, and R. Okazaki, *Organometallics*, **15**, 4531 (1996).

[4] H. Puff, R. Gattermayer, R. Hundt, and R. Zimmer, *Angew. Chem., Int. Ed. Engl.*, **16**, 547 (1977).