

## A CONVENIENT PREPARATION OF ARYLTHIOSTANNANES

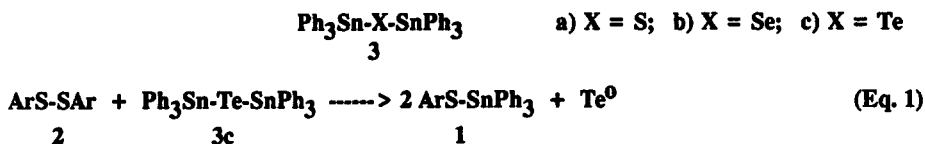
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*Summary: Arylthiostannanes 1 can be prepared in excellent yield by the reaction of diaryldisulfides 2 with bis(triphenylstannyl)telluride (3c) under mild conditions. In addition, the use of telluride 3c with aryl disulfides in the presence of fluoride ion and benzyl bromide gives a one-pot synthesis of unsymmetrical sulfides.*

Alkyl- and arylthiostannanes 1 have been recognized as useful aryl/alkyl sulfur transfer reagents for the preparation of thiol esters<sup>1</sup>, thiosulfinate esters,<sup>2</sup> N-alkylthio- and N-arylthioimides,<sup>3</sup> thioglycosides,<sup>4</sup> organic disulfides,<sup>5</sup> and unsymmetrical organic sulfides.<sup>6</sup> However, the synthesis of these thiostannanes utilizes the reaction of odorous thiols with organotin chlorides, organotin hydrides or organotin oxides.<sup>7</sup>

Our recent discovery of a mild desulfurization of organic trisulfides to give organic disulfides upon the reaction with bis(triphenylstannyl)chalcogenides 3 led us to explore the reaction of these reagents with organic disulfides.<sup>8</sup>

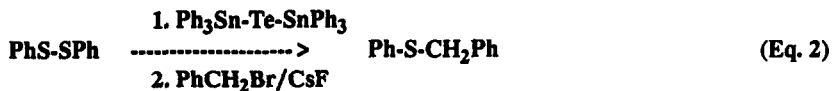


Here we report that unlike the desulfurization reaction with its trisulfide analogs, the reaction of aryl disulfides with bis(triphenylstannyl)telluride (3c) gives exclusively the arylthiostannanes 1 in high yield (Eq. 1, Table 1). Bis(triphenylstannyl)selenide (3b) was also effective for the reaction, except that it was much less reactive than the corresponding telluride. A variety of arylthiostannanes were prepared in excellent isolated yields (Table 1). Under the same reaction conditions, alkyl and benzyl disulfides failed to react in a variety of solvents (e.g. benzene, chloroform, THF, acetonitrile).

A typical preparative procedure is as follows and illustrates the small scale of reaction that is possible. A solution of ditolyl disulfide (25 mg, 0.1 mmol) in 10 mL of dried acetonitrile (CaH<sub>2</sub>) was purged with a flow of nitrogen for 5 min. To the solution, bis(triphenylstannyl)telluride (4a, 83 mg, 0.1 mmol) was added in one portion. A black deposit formed immediately. The reaction mixture was stirred at room temperature for 3h. Evaporation of the solvent left a black residue. Extraction of the residue with CCl<sub>4</sub> with filtration through celite gave a clear solution.

Evaporation of the solvent gave a colorless syrup which crystallized upon the addition of ethanol to give a white solid. Recrystallization of the solid from CCl<sub>4</sub> and ethanol produced pure triphenyl tolylthiostannane (40 mg, 85%) characterized both by <sup>1</sup>H NMR and mp 102-104°C (Lit.<sup>7</sup> 103-105°C).

In the case of the reaction of diphenyl disulfide with telluride 3c, the phenylthiostannane which was prepared was transformed, without isolation, to phenyl benzyl sulfide by its reaction with benzyl bromide<sup>6</sup> (Eq. 2). In sum, this chemistry provides a simple and very mild way to convert aryl disulfides into the versatile thiostannanes 1; in addition it affords one-pot access to unsymmetrical aryl thioethers in very good yield (Table 1).



**Table 1. Preparation of Thiostannanes from Organic Disulfides**

Entry	Disulfide	Reagent	Time(h)	Product	Yield(%) <sup>a</sup>
1	(p-MePhS) <sub>2</sub>	3c	3	p-MePhS-SnPh <sub>3</sub>	85(quant.)
2	(p-MePhS) <sub>2</sub>	3b	3	p-MePhS-SnPh <sub>3</sub>	(28)
3	(p-ClPhS) <sub>2</sub>	3c	3	p-ClPhS-SnPh <sub>3</sub>	83
4	(p-FPhS) <sub>2</sub>	3c	3	p-FPhS-SnPh <sub>3</sub>	quant. <sup>b</sup>
5	(2-NaphS) <sub>2</sub>	3c	5	2-NaphS-SnPh <sub>3</sub>	81
6	(PhS) <sub>2</sub>	3c	5	PhS-SnPh <sub>3</sub>	92 <sup>c</sup>
7	(PhCH <sub>2</sub> S) <sub>2</sub>	3c	24	PhCH <sub>2</sub> S-SnPh <sub>3</sub>	(0)

All the reactions were carried out at room temperature in acetonitrile; all the compounds are known; entries 1, 3 and 5 have the same m.p. as literature reports; <sup>a</sup> isolated yield; H NMR yield in parenthesis; <sup>b</sup> F NMR yield; <sup>c</sup> yield of PhSCH<sub>2</sub>Ph by alkylation with PhCH<sub>2</sub>Br.

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#### References

1. D. N. Harpp, T. Aida, and T. H. Chan, *Tetrahedron Lett.*, 2853 (1979); S. Kozuka, I. Naribayashi, *Bull. Chem. Soc., Jpn.* 52, 3638 (1979).
2. D. N. Harpp, T. Aida and T. H. Chan, *Tetrahedron Lett.*, 24, 5173 (1983).
3. D. N. Harpp, T. Aida, J. DeCesare, P. Tisnes and T. H. Chan, *Synthesis*, 1037, (1984)
4. K. Kohata, and H. Meguro, *Agric. Biol. Chem.* 46, 2077 (1982); T. Ogawa, S. Nakabayashi, and K. Sasajima, *Carbohydrate Res.* 95, 308 (1981); T. Ogawa, and M. Matsui, *Carbohydrate Res.* 54, C17, 1977.
5. D. N. Harpp, S. J. Bodzay and T. Aida, *Tetrahedron Lett.* 27, 441 (1986); N. Yamazaki, S. Nakahama and T. Yamaguchi, *Chem. Lett.*, 1355 (1980); J. L. Wardell, P. L. Clarke, *ibid* 26, 345 (1971); J. L. Wardell, and D. W. Grant, *J. Organomet. Chem.* 20, 91 (1969).
6. D. N. Harpp and M. Gingras, *Tetrahedron Lett.*, 28, 4373 (1987); K. Itoh, I. K. Lee, I. Matsuda, S. Sakai, Y. Ishii, *Tetrahedron Lett.*, 2667 (1967); K. Itoh, K. Matsuzaki and Y. Ishii, *J. Chem. Soc. C2709* (1968); S. Kozuka and S. Ohya, *Bull. Chem. Soc. Jpn.*, 51, 265 (1978); 1 and *J. Organomet. Chem.*, 149, 161 (1978)
7. M. Pereyre, J. P. Quintard, and A. Rahm, "Tin in Organic Synthesis", Butterworths & Co., p. 14, 1987; J. L. Talley, A. M. Colley, *ibid.*, 215, C38 (1981); W. E. Davidson, K. Hills, M. C. Henry, *J. Organomet. Chem.* 8, 19 (1967); M. Wieben, M. Schmidt, *ibid.*, 1, 336 (1964).
8. C. J. Li and D. N. Harpp, *Tetrahedron Lett.*, 33, 0000 (1992), *in press*; for other uses of this reagent, see: C.-J. Li and D. N. Harpp, *Tetrahedron Lett.*, 32, 1545 (1991); C.-J. Li and D. N. Harpp, *Sulfur Lett.*, 13, 139 (1991); C.-J. Li and D. N. Harpp, *Tetrahedron Lett.*, 31, 6291 (1990).

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