Tetrahedron Letters, Vol. 33, No. 48, pp. 7293-7294, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

A CONVENIENT PREPARATION OF ARYLTHIOSTANNANES

C.-J. LI AND DAVID N. HARPP*

Department of Chemistry
801 Sherbrooke St. W.
McGill University
Montreal, Quebec, Canada H3A 2K6

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[1], thiosulfinate esters,[2] N-alkylthio- and N-arylthioimides,[3] thioglycosides,[4] organic disulfides,[5] and unsymmetrical organic sulfides.[6] However, the synthesis of these thiostannanes utilizes the reaction of odorous thiols with organotin chlorides, organotin hydrides or organotin oxides.[7]

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.[8]

$$\underset{\mathbf{3}}{\mathrm{Ph_3Sn\text{-}X\text{-}SnPh_3}} \qquad \text{a) X = S; b) X = Se; c) X = Te}$$

$$\underset{\mathbf{2}}{\mathrm{ArS\text{-}SAr}} + \underset{\mathbf{3c}}{\mathrm{Ph_3Sn\text{-}Te\text{-}SnPh_3}} \text{------>} \underset{\mathbf{1}}{\mathrm{2\,ArS\text{-}SnPh_3}} + \mathrm{Te^0} \qquad \text{(Eq. 1)}$$

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_2) 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_4 with filtration through celite gave a clear solution.

Evaporation of the solvent gave a colorless syrup which crystalized upon the addition of ethanol to give a white solid. Recrystallization of the solid from CCl^4 and ethanol produced pure triphenyl tolylthiostannane (40 mg, 85%) characterized both by ^1H NMR and mp 102-104°C (Lit.[7] 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[6] (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).

$$\mathrm{PhS\text{-}SPh} \xrightarrow[\text{2. PhCH}_2\text{Br/CsF}]{\text{1. Ph}_3\text{Sn-Te-SnPh}_3} \mathrm{Ph\text{-}S\text{-}CH_2Ph} \qquad \text{(Eq. 2)}$$

Table 1. Preparation of Thiostannanes from Organic Disulfides

Entry	Disulfide	Reagent	Time(h)	Product	Yield(%)[a]
1	$(p\text{-MePhS})_2$	3c	3	$p\text{-MePhS-SnPh}_3$	85(quant.)
2	$(p\text{-MePhS})_2$	3b	3	$p\text{-MePhS-SnPh}_3$	(28)
3	$(p\text{-ClPhS})_2$	3c	3	$p\text{-ClPhS-SnPh}_3$	83
4	$(p\text{-FPhS})_2$	3c	3	$p\text{-FPhS-SnPh}_3$	quant.[b]
5	$(2\text{-NaphS})_2$	3c	5	2-NaphS-SnPh_3	81
6	$(\text{PhS})_2$	3c	5	PhS-SnPh_3	92[c]
7	$(\text{PhCH}_2\text{S})_2$	3c	24	$\text{PhCH}_2\text{S-SnPh}_3$	(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; [a] isolated yield; H NMR yield in parenthesis; [b] F NMR yield; [c] yield of PhSCH_2Ph by alkylation with PhCH_2Br.

Acknowledgements

We thank the F.C.A.R. (Québec) and the Natural Sciences and Engineering Research Council of Canada for financial support.

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).

(Received in USA 24 July 1992; accepted 1 September 1992)