

Preliminary communication

RHODIUM CATALYZED DEHYDROGENATION OF TRIORGANOTIN HYDRIDES AND MERCAPTANS, PREPARATION OF TRIORGANOTIN MERCAPTIDES

JOHN J. TALLEY* and ALICE M. COLLEY

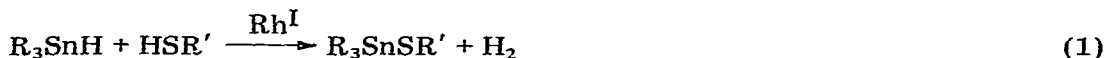
Chemical Synthesis Branch, Chemical Synthesis & Engineering Laboratory, General Electric Corporate Research and Development Center, Schenectady, New York 12301 (U.S.A.)

(Received March 16th, 1981)

Summary

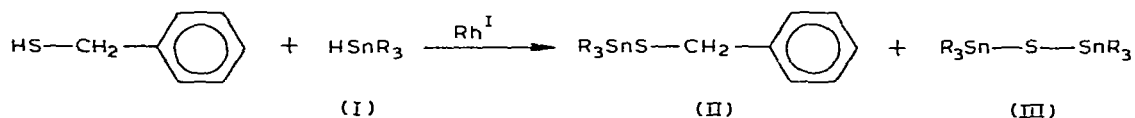
Triorganotin hydrides react with a variety of aliphatic and aromatic mercaptans in the presence of a catalytic amount of chlorotris(triphenylphosphine)rhodium to produce triorganotin mercaptides.

Trialkyltin mercaptides have recently been reported as convenient reagents for the preparation of thiol esters from acid chlorides [1]. Triorganotin mercaptide derivatives have been prepared by the action of metal mercaptides on trialkyltin halides [2], or by the reaction of mercaptans with triorganotin oxides [3] and triorganotin alkoxides [4]. We now wish to report that triorganotin hydrides react with mercaptans in the presence of chlorotris(triphenylphosphine)rhodium to produce triorganotin mercaptides and hydrogen in high yield (eq. 1).



The uncatalyzed reaction of tri-*n*-butyltin hydride with thiophenol occurs at 25°C to the extent of ca. 3% after 2 h, whereas in the presence of 0.1 mole percent chlorotris(triphenylphosphine)rhodium the reaction is complete in 30 min. The rate of reaction was dependent upon the nature of both the mercaptan and tin hydride. Primary thiols were more reactive than secondary and tertiary mercaptans.

Treatment of benzylmercaptan with triphenyltin hydride (Ia) in the presence of one-half mole percent chlorotris(triphenylphosphine)rhodium resulted in the formation of a 1/10 mixture of triphenyltin benzylmercaptide (IIa), and bis(triphenyltin)sulfide (III) [5]. Tri-*n*-butyltin hydride reacted with benzylmercaptan

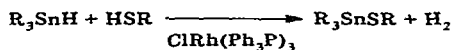
(a) R = C₆H₅(b) R = n-C₄H₉

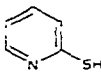
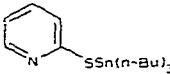
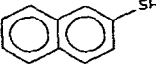
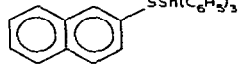
to produce only tri-*n*-butyltin benzylmercaptide (IIb); we have not observed the formation of bis(tri-*n*-butyltin) sulfide (IIIb) in any of these reactions. The uncatalyzed reaction between benzylmercaptan and triphenyltin hydride [5] at 160°C gave only bis(triphenyltin) sulfide.

In a typical procedure, 2.20 g (20 mmol) of thiophenol, 5.82 g (20 mmol) of tri-*n*-butyltin hydride in 50 ml of tetrahydrofuran under nitrogen was treated with 50 mg (0.25 mol%) chlorotris(triphenylphosphine)rhodium. Hydrogen was evolved at a very rapid rate for ca. 10 min. After the reaction mixture had been kept at room temperature for an additional 20 min, the solvent was removed under reduced pressure and the product vacuum distilled to give 7.25 g,

TABLE 1

PREPARATION OF TRIORGANOTIN MERCAPTIDES



| Mercaptan | Triorganotin hydride | Catalyst level (mol%) | Reaction conditions | Product | Yield ^d | B.p. (°C/mmHg) ^c (m.p. (°C)) |
|--|---|-----------------------|---------------------|---|--------------------|---|
| C ₆ H ₅ SH | n-Bu ₃ SnH | 0.25 | 20°C, 30 min | C ₆ H ₅ SSn(n-Bu) ₃ | 90 | 165–170/1.0 |
| C ₆ H ₅ CH ₂ SH | n-Bu ₃ SnH | 0.1 | 25°C, 20 min | C ₆ H ₅ CH ₂ SSn(n-Bu) ₃ | 92 | 145/0.15 |
| n-BuSH | n-Bu ₃ SnH | 0.1 | 25°C, 20 min | n-BuSSn(n-Bu) ₃ | 85 | 165/0.55 |
| <i>i</i> -PrSH | n-Bu ₃ SnH | 0.1 | 70°C, 1 h | <i>i</i> -PrSSn(n-Bu) ₃ | 95 | 115/0.15 |
| <i>t</i> -BuSH | n-Bu ₃ SnH | 0.1 | 90°C, 4 h | <i>t</i> -BuSSn(n-Bu) ₃ | 72 | 162/0.5 |
|  | n-Bu ₃ SnH | 0.1 | 60°C, 30 min |  | 78 | 183–186/1.0 |
| C ₆ H ₅ SH | (C ₆ H ₅) ₃ SnH | 0.5 | 50°C, 3 h | C ₆ H ₅ SSn(C ₆ H ₅) ₃ | 77 | (99–101) |
| C ₆ H ₅ CH ₂ SH | (C ₆ H ₅) ₃ SnH | 0.5 | 85°C/30 min | C ₆ H ₅ CH ₂ SSn(C ₆ H ₅) ₃ ^d (C ₆ H ₅) ₃ SnSSn(C ₆ H ₅) ₃ | 77 ^b | (83–84) (144.0–144.5) |
| n-BuSH | (C ₆ H ₅) ₃ SnH | 0.5 | 65°C, 4 h | n-BuSSn(C ₆ H ₅) ₃ | 72 | oil ^e |
| <i>i</i> -PrSH | (C ₆ H ₅) ₃ SnH | 0.25 | 65°C, 8 h | <i>i</i> -PrSSn(C ₆ H ₅) ₃ | 70 | (82.0–82.5) |
| <i>t</i> -BuSH | (C ₆ H ₅) ₃ SnH | 0.5 | 95°C, 3 h | <i>t</i> -BuSSn(C ₆ H ₅) ₃ ^d (C ₆ H ₅) ₃ SnSSn(C ₆ H ₅) ₃ | b | (131.5–133.0) (144–145) |
|  | (C ₆ H ₅) ₃ SnH | 0.5 | 90°C, 4 h |  | 85 | (93.5–95.5) |

^aIsolated/purified yields. ^bBis(triphenyl)tin sulfide was the major product. ^cAll new compounds gave satisfactory IR, NMR, and high resolution mass spectral data and were compared to authentic samples prepared independently from the triorganotin halides and the corresponding mercaptan and found to be identical in all respects. ^dPurified by column chromatography on silica gel (using hexane as eluant). ^eDecomposition took place upon attempted distillation.

95%, of tri-*n*-butyltin phenyl sulfide, b.p. 165–170°C/1.0 mmHg, lit. [3] b.p. 147°C/0.2 mmHg.

As can be seen from Table 1, the yields are good, the reaction is rapid and the reaction conditions mild. A wide variety of mercaptans can be readily converted to triorganotin mercaptides by this method, and the work-up simply involves removal of the solvent (if any), and either distillation or crystallization of the crude product. This procedure is particularly useful for the preparation of tri-*n*-butyltin mercaptides.

References

- 1 D.N. Harpp, T. Aida, and T.H.Chan. *Tetrahedron Lett.*, (1979) 2853.
- 2 R.C. Mehrotra, Y.D. Gupta, and D. Sukhani. *Ind. J. Chem.*, 7 (1969) 708.
- 3 M.E. Peach. *Can. J. Chem.*, 46 (1968) 211.
- 4 R.C. Mehrotra, V.D. Gupta, and D. Sukhani. *J. Organometal. Chem.*, 7 (1967) 85.
- 5 M. Pang and E.I. Becker. *J. Org. Chem.*, 29 (1964) 1948.