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A simple synthesis of hexamethyldistannane from bis(trimethylstannyl)sulphide

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Abstract

A new and cheap synthesis of hexamethyldistannane has been devised starting from bis(trimethylstannyl)sulphide, itself prepared according a new method.

Introduction

New efficient stannylating agents and new methods for their preparation provide the basis for much development of organotin chemistry, particularly with respect to applications in organic synthesis [1].

Hexamethyldistannane (**1**) has recently found a range of uses as stannylating reagent [2] and is also a useful precursor of trimethylstannyllithium free from Li metal [3]. The distannane is commercially available [4] but rather expensive, and the only synthesis fully described in the literature is relatively complex and in our hands sometimes failed to give the expected results in terms of the yields and purities of the product [5].

Very recently a simple synthesis of hexaalkyldistannanes (but not with methyl as the alkyl group) involving deoxygenation of the corresponding oxides was described [6]. In the hope of finding an easy, reproducible, and low cost preparation of the distannane we decided to investigate the possibility to obtaining it by desulphurization of bis(trimethylstannyl)sulphide [7] (**2**), as shown in eq. 1. in which M^0 denotes a metal.

$$\underset{(\mathbf{2})}{(Me_3Sn)_2S} \xrightarrow{M^0} \underset{(\mathbf{1})}{Me_3SnSnMe_3} \qquad (1)$$

Compound **2** was prepared [8] in high yields (up to 90% of isolated product), by

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Table 1

Conditions for the preparation of **1**

Desulphurization reagent	Na/**2** ratio	Solvent	Time for complete disappearance of **1** (h)
Na/Hg amalgam	30/1	boiling THF	24
Na	4/1	boiling THF	24
Na	3/1	boiling benzene	12
Na	4/1	neat, 110 °C	6
Na	4/1	boiling 2-picoline	40 min

treating Me_3SnCl with Li_2S generated in THF solution from sulphur and $Li(BEt_3)H$ [9], as shown in eqs. 2 and 3.

$$2\ Li(BEt_3)H + S \rightarrow Li_2S_{(THF)} + H_2 + 2\ BEt_3 \qquad (2)$$

$$Li_2S_{(THF)} + 2\ Me_3SnCl \rightarrow \underset{(\mathbf{2})}{(Me_3Sn)_2S} + 2\ LiCl \qquad (3)$$

The same result was achieved by generation of the sulphide ion from sulphur and $NaBH_4$ in THF, followed by addition of Me_3SnCl. Although this method gives lower yields of the stannyl sulphide (60% of isolated product), it has advantages over the use of $Li(BEt_3)H$ in terms of safety and lower cost.

Desulphurization of **2** with Na to give **1** was carried out under various conditions as indicated in Table 1.

$$\underset{(\mathbf{2})}{(Me_3Sn)_2S} \xrightarrow{Na} \underset{(\mathbf{1})}{Me_3SnSnMe_3} + Na_2S \qquad (4)$$

In all cases the progress of the reaction was monitored by GLC analysis. This analysis did not reveal the presence of any other products in the reaction mixture.

As shown in Table 1 the simplest conditions were those used in entries 2 and 4, and larger scale reactions were carried out only for these conditions, and gave **1** in 45–50% yields of isolated product.

Other metals and reducing agents were also tried. Compound **2** does not react with activated Mg in refluxing THF, whereas with $LiAlH_4$ or Raney/Ni it gives unidentified volatile products with no evidence for formation of **1**.

The reaction between sulphide **2** and Na has proved to provide a very satisfactory method for the preparation of **1** in terms of purity (no traces of polystannanes were detected), and eases of work up.

A study on the potential of **2** as a stannylating agent is under-way in our laboratory.

Experimental

Bis(trimethylstannyl)sulphide (2) from Li(BEt$_3$)H and sulphur

To a suspension of sulphur (1.21 g, 38 mmol) in dry THF (5 ml) lithium triethylborohydride (38 ml of a 1 *M* solution in THF, 38 mmol) was added slowly at room temperature. After 1 h of stirring at room temperature trimethylstannyl chloride (7.6 g, 38 mmol) in dry THF (5 ml) was added. After a further 1 h of stirring the mixture was diluted in pentane (200 ml). The precipitate formed was filtered off through neutral aluminium oxide. After evaporation of the solvent from the filtrate, **1** was isolated by fractional distillation (5.7 g, 83%) b.p. 51–52 °C at 0.05 mm Hg.

^{1}H NMR ($CDCl_3$) 0.39 (s). ^{13}C NMR ($CDCl_3$) −2.42 (s). ^{119}Sn NMR ($CDCl_3$) 189.27 (s). MS (m/e) 362 (M^+), 347, 330, 165 (base), 135.

*Bis(trimethylstannyl)sulphide (**1**) from sodium borohydride and sulphur*

Sulphur (1.2 g, 37.5 mmol) was added to a dispersion of sodium borohydride (0.95 g, 25 mmol) in dry THF (10 ml), at room temperature and the mixture was stirred for 1 h. Trimethylstannyl chloride (5 g, 25 mmol) in dry THF (5 ml) was than added, and the mixture stirred for 24 h. Pentane (250 ml) was then added, and the precipitate formed was filtered off through neutral aluminum oxide. The solvent was evaporated from the filtrate and fractional distillation of the residue gave **2** (2.8 g, 61%).

Hexamethyldistannane 1

Preparation in THF. Bis(trimethylstannyl)sulphide (0.9 g, 2.5 mmol) and sodium (0.057 g, 2.5 mmol) were mixed in dry THF (3 ml) and the mixture was refluxed for 24 h, during which the addition of sodium (2.5 mmol each time) was repeated three times at 1 h intervals. The mixture was subsequently filtered through dry sodium sulphate which was washed several times with dry THF. Evaporation of the filtrate left **1**, which was isolated by fractional distillation. (0.350 g, 50%) b.p. 150 °C at 25 mm Hg. It was identified by GLC comparison with a commercial sample.

Preparation without solvent. Bis(trimethylstannyl)sulphide (0.9 g, 2.5 mmol) and sodium (0.180 g, 7.5 mmol) were stirred in a Kugelrohr apparatus at 110 °C for 6 h. Distillation under vacuum then gave **1** (0.270 g, 45%).

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