Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

Thiocarbonylation and iminocarbonylation reactions of 2-mercaptoethanol via its bis(tributyltin) derivatives

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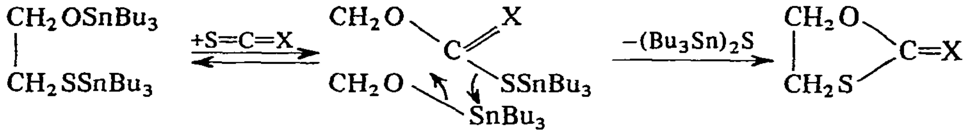
(Received August 24th, 1970)

Although thiocarbonylation of 2-mercaptoethanol by thiophosgene to afford 1,3-oxathialane (IIIa) has been reported[1], Jones and Andreades failed in their attempt, to repeat the reaction. However, they succeeded in preparing compound (IIIa) in 46% yield from a lead salt of 2-mercaptoethanol and thiophosgene. In our previous papers[3,4], we reported novel thiocarbonylation reactions of diols, alkanolamines, and diamines by reaction of their bis(tributyltin) derivatives with carbon disulfide at low temperature; although bis(tributyltin) 2-mercaptoethanolate (I) could react with carbon disulfide reversibly and exothermically at room temperature, the starting material (I) and its decomposition product, the dimer of 2-dibutylstanna-1,3-oxathialane, were obtained on distillation[4,5]. We assumed that the intermediate (II) would fail to cyclize, owing to the reactivity of the Sn–S bond in (II) being less than those of the corresponding Sn–O and Sn–N bonds.



(1)

(I) (II) (IIIa), X = S
(IIIb), X = NPh

In this communication, we report the reaction of *O,S*-bis(tributyltin) 2-mercaptoethanolate (I) with carbon disulfide at a higher reaction temperature, above 45° (higher than the boiling point of carbon disulfide), in a sealed system, which afforded a good yield of (IIIa).

The bis(tributyltin) compound (I) (14.8 mmol) and carbon disulfide (16.2 mmol) were allowed to react for 20 h at 60° under dry nitrogen in a sealed glass tube. The reaction mixture was separated by column chromatography to give a 65% yield of (IIIa), 57% yield of bis(tributyltin) sulfide, and 35% yield of the tributyltin derivative of 2-mercaptoethanol.

The structure of the isolated product (IIIa), b.p. about 65–70°/0.2 mm (with partial decomposition), was identified by IR (ν(C=S) 1180 cm^{-1}), NMR (τ(CH_2O) 5.02, τ(CH_2S) 6.28, J = 7.2 Hz in $CHCl_3$), mass spectrometry (m/e 120), and analysis (Found: C, 29.96; H, 3.50. $C_3H_4O_2S$ calcd.: C, 29.98; H, 3.35%). The reaction rate was relatively low below the boiling point of carbon disulfide. On the other hand, some decomposition of (IIIa) occurred at 80–100°, and the yield of (IIIa) in the reaction at 80° was low (about 20%). The optimum temperature range required for reaction (1) (X = S) was about 45–65°, indicating that the linear bis(tributyltin) compound (I) is an unexpectedly reactive liquid, as compared with the dimeric solids 2-dibutylstanna-1,3-thioxolane and 1,3-dioxolane[6].

Whereas in Jones and Andreades' method a toxic and troublesome reagent, thiophosgene, was used, in our method, carbon disulfide acts as a useful thiocarbonylating reagent, and moreover the starting material (I) is easily prepared from ethylene thiolcarbonate and bis(tributyltin) oxide[5] or from 2-mercaptoethanol and tributyltin amide[7] or alkoxide[8]. Furthermore, reaction (1) has the merit of high selectivity.

Bis(tributyltin) compound (I) also reacted with phenyl isothiocyanate for 20 h at 60°, and afforded a 49% yield of ethylene thiol-phenyliminocarbonate (IIIb) (X = NPh), m.p. 65.5–66.5° (lit.[5] 65.0–65.5°).

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