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Note Synthesis of triphenyltin(IV) hydrosulfide

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Compounds of the type R₃SnSH are believed to be unstable (unless sterically protected by very bulky R

ABSTRACT

reported.

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© 2010 Elsevier B.V. All rights reserved. Designing and synthesis of hydrosulfido complexes have at-Our attempt to synthesize Ph₃SnSH by passing H₂S gas to a suspentracted a lot of attention over last two decades owing to their fassion of triphenyltin hydroxide was expectedly unsuccessful as the cinating structures, biological and catalytic properties [1–6]. product was bis-triphenyltin sulfide. Similarly, bubbling a stream of H₂S gas into a solution of triphenyltin chloride and triethyl-Metal-sulfur bonding is of importance in bioinorganic [7–9] and biomimetic chemistry [10-16] and the chemistry of SH-containing amine also gave the same product due to facile condensation of complexes is of relevance to metal sulfide hydrosulfurization catathe desired hydrosulfide. lysts [6,7]. Metal hydrosulfide complexes act as precursors for the preparation of heterobimetallic complexes and clusters [17,18]. A number of hydrosulfide complexes of transition metals are known

Though there is no thermochemical data available for such reactions the Sn-S and S-H bonds are well known to be thermally stable [25]. However, the heat evolved during the formation of R₃SnSH is possibly enough to cross the energy barrier for the next condensation step. If this presumption is true then any alternative route which is endothermic (or less exothermic) should give the hydrosulfide compound without its further condensation.

groups) because of their facile condensation into the corresponding sulfide, $(R_3Sn)_2S$. One such com-

pound, Ph₃SnSH has been synthesized by an one pot reaction of triphenyltin hydroxide with thiophos-

gene followed by the hydrolysis of the intermediate triphenyltin chlorothioformate. The product,

triphenyltin hydrosulfide has been characterized by IR, ¹H, ¹³C and ¹¹⁹Sn NMR spectral techniques. Single crystal X-ray analysis revealed that the molecule is a discrete monomer containing tin atom at the centre

of a distorted tetrahedron. Plausible reaction mechanism for the formation of the molecule has also been

With this view, we tried to find out an entirely different route [27]. Triphenyltin hydroxide in presence of triethylamine was treated with thiophosgene (CAUTION! Toxic) so that it formed triphenvltin chlorothionformate which then underwent a S_{Ni} reaction forming the corresponding chlorothiolformate. The later was then hydrolyzed leading to the formation of triphenyltin hydrosulfide and chloroformic acid. Chloroformic acid being unstable decomposed into carbon dioxide and hydrochloric acid. As we have seen earlier, in case of organotin thiocarboxylates hydrolysis may cleave the Sn–S bond and S–C bond. However, acidic medium not only facilitates cleavage of the S-C bond but also impedes formation of another weak acid (H₂S) and thus the condensation of the hydrosulfide groups to form organotin sulfide. The step wise mechanism is shown in Scheme 1.

An alternative mechanism may involve the slow hydrolysis of thiophosgene [29] giving H₂S, HCl and CO₂ followed by the subsequent reaction of Ph₃SnOH with H₂S. The *in situ* generation of H₂S

but analogous compounds of main group metals are scarce. The main problem associated with the synthesis of hydrosulfide

complexes is their tendency to aggregated further leading to the

formation of di/polynuclear sulfide complexes and sometimes to

insoluble metal sulfides [1,19]. However, a few tin hydrosulfides

are known which have been stabilized by either steric protection

using highly bulky substituents or at a hypervalent tin centre

[19.20]. Very recently, we could isolate a hydrosulfidotin complex

in a rigid polymeric framework by controlled hydrolysis of a dior-

ganotin thiocarboxylate [21]. In spite of all these, compounds of

the type R₃SnSH are believed to be non-isolable as they undergo

condensation reaction during their synthesis leading to formation

of organotin sulfides (R₃SnSSnR₃) [19,22]. Here, we report on a

novel method of synthesis of a triorganotin hydrosulfide without

incorporation of any appreciable steric protection which is ex-

pected to be a very useful precursor for bi/polynuclear complexes.

compounds results into corresponding organotin sulfides [23,24].

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It is well known that a reaction of H₂S with organotin

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Scheme 1. Pluasible mechanism for the formation of Ph₃SnSH.

may lead to the formation of Ph₃SnSH very slowly thereby lowering the chances of further condensation into triphenyltin sulfide. However, the formation of triphenyltin chlorothionformate [Ph₃SnOC(S)Cl] suggested in Scheme 1 are in accordance with those reported for conversion of phenols to corresponding thiophenols [30].

The molecular structure of Ph₃SnSH is shown [31] in Fig. 1. The geometry around Sn is approximately tetrahedral. The Sn1–S01 bond length 2.359(2) Å is slightly shorter than those in $(Ph_3Sn)_2S$ (2.397 Å) [34] and is comparable to that in Me₂Sn(SH)(O₂CMe) [21]. Except SH⁺⁺HC there is no other intermolecular contact of significance. Intermolecular Sn–Sn and Sn–S distances are quite large being 6.221 and 5.861 Å, respectively.



Fig. 1. ORTEP view of Ph₃SnSH.

In solution also the discrete molecular structure is retained as evinced by presence of a 119 Sn NMR peak at 81.43 ppm which is indicative of a tetra-coordinated tin. The C–Sn–C bond angle in solution could be estimated to be 108.9° from the 1 J(119 Sn– 13 C) value [35].

Acknowledgments

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Appendix A. Supplementary materials

CCDC 755649 contains the supplementary crystallographic data forPh₃SnSH. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica. 2010.12.014.

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- [27] To a stirred suspension of Ph₃SnOH (1.100 g, 3.0 mmole) and Et₃N (0.303 g, 3.0 mmole) in benzene (10.0 mL), added a solution of CSCl₂ (0.345 g, 3.0 mmole) in benzene (5.0 mL) with stirring at ~6 °C. The reaction mixture was further stirred for 4 h maintaining the temperature below 10 °C. Water (0.054 g, 3.0 mmole) was added to the reaction mixture which was then stirred for 1 h at room temperature (~30 °C) followed by filtration of the precipitated mass (1.01 g). The filtrate was dried under reduced pressure and the residue was dissolved in diethyl ether, filtered and left overnight for crystallization. A crop of colorless crystals suitable for X-ray diffraction was obtained. Yield: 0.113 g (10%). Mp 90–92 °C. Anal. Calc. for C₁₈H₁₆SSn: C, 56.43; H, 4.21. Found: C, 56.27; H, 4.14%. ¹H NMR (CDCl₃, TMS at δ = 0.) 1.25 (SH), 7.25–7.77 (Ph). ¹³C NMR: 128.59–137.86 (Ph). ¹¹⁹Sn (Me₄Sn at δ = 0): 81.43. IR (KBr): v(S–H) too weak to be observed [28].

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structure were collected on a Bruker SMART APEX CCD diffractometer. The structures were solved by direct methods (Shelxs-97) and then refined on F^2 by the full matrix least-squares technique with the SHELXL-97 software [32] using WinGX program package [33].

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