

Communications

A Thermal Reductive-Elimination Route to Perbutylated Cyclopolystannanes

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Summary: Thermolysis of dibutyl(2-ethoxyethyl)stannane (**4**) in heptane at 150 °C quantitatively provides the perbutylated cyclopolystannanes (Bu₂Sn)₅ (**1**) and (Bu₂Sn)₆ (**2**). Trapping experiments reveal that this thermal reductive-elimination process proceeds in a stepwise manner, involving the generation of a trivalent tin intermediate that then undergoes an unprecedented β-elimination reaction.

Recently, Joussemaume and co-workers¹ have shown that mixtures of the perbutylated five- and six-membered-ring polystannanes (Bu₂Sn)_n (n = 5 and 6; **1** and **2**, respectively) can function as efficient air-activated catalysts for silicone curing. At the present time, these mixtures are prepared through either the palladium-catalyzed cyclodehydrogenation of dibutylstannane (**3**) or the alkali-metal reduction of dibutyltin dichloride.^{1,2} Although high yielding, both of these metal-mediated processes possess certain technical disadvantages with respect to either precursor stability and/or product isolation. Accordingly, this prompted us to consider whether an alternative metal-free route to peralkylcyclopolystannanes could be developed: in particular, one that might allow these compounds to be accessed through a thermal process. If successful, this route might then serve as the basis for the development of

new classes of thermally activated latent catalysts.³ Herein, we present preliminary results which show that the first part of this objective has now been successfully met.

It has previously been reported that a mixture of perbutylated cyclopolystannanes can be obtained in high yield through the cocondensation reaction between **3** and dibutyltin dimethoxide that occurs rapidly at room temperature according to Bu₂SnH₂ + Bu₂Sn(OMe)₂ → 2n(Bu₂Sn)_n + 2MeOH.^{4,5} The proposed initial step in this reaction is the formation of the unstable intermediate Bu₂SnH(OMe), which then undergoes rapid cyclocondensation. It has also been documented that group 14 organometallic compounds bearing alkyl substituents which incorporate an electronegative group, X (e.g., Cl, OH, or OCOR), in the β-position are thermally unstable and can undergo facile metal-carbon bond cleavage through a process that liberates an alkene and generates a new M-X bond (i.e., β-elimination).^{3,6} Thus, on the basis of these two observations, the new thermal

(3) (a) Joussemaume, B.; Gouron, V.; Maillard, B.; Pereyre, M.; Francés, J.-M. *Organometallics* **1990**, *9*, 1330. (b) Joussemaume, B.; Noiret, N.; Pereyre, M.; Francés, J.-M.; Pétraud, M. *Organometallics* **1992**, *11*, 3910.

(4) Neumann, W. P.; Schneider, B. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 751.

(5) Although the exact identities of the polystannane products were not originally specified, we have determined by ¹¹⁹Sn NMR spectroscopy that **1** and **2** are the sole cyclopolystannane products that are formed at room temperature by this route, together with a number of additional coproducts containing the Sn-H functionality.

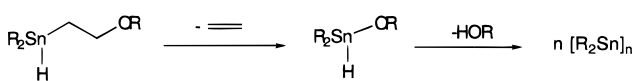
(6) (a) Davidson, I. M. T.; Jones, M. R.; Pett, C. *J. Chem. Soc. B* **1967**, 937. (b) Kauffmann, T.; Kriegesmann, R.; Hamsen, A. *Chem. Ber.* **1982**, *115*, 1818.

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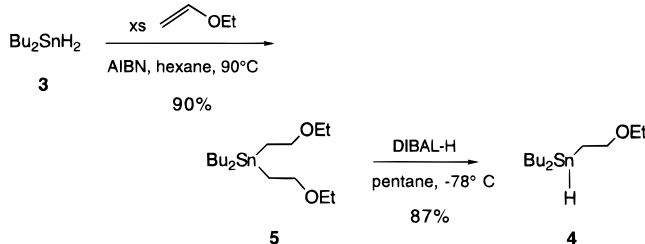
(1) Joussemaume, B.; Noiret, N.; Pereyre, M.; Saux, A. *Organometallics* **1994**, *13*, 1034.

(2) Depending on reaction conditions, these methods have been shown to provide varying ratios of **1** to **2** in the range of 90/10 to 30/70.

Scheme 1



Scheme 2



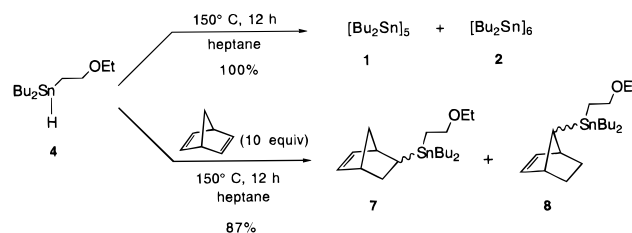
AIBN = 2,2'-azobis(2-methylpropionitrile)
DIBAL-H = diisobutylaluminum hydride

route to cyclopolystannanes shown in Scheme 1 was envisioned.

In order to substantiate the viability of the general design strategy of Scheme 1, the solution thermolysis of dibutyl(2-ethoxyethyl)stannane (**4**)⁷ was investigated. As shown in Scheme 2, this compound was easily prepared on a large scale through a two-step process involving the hydrostannation of ethyl vinyl ether with **3** to produce bis(2-ethoxyethyl)dibutylstannane (**5**), followed by monoelimination of one of the 2-ethoxyethyl substituents of **5** with diisobutylaluminum hydride (DIBAL-H)⁸ to generate **4**.^{9,10}

Satisfactorily, when a 0.32 M solution of compound **4** in heptane was heated to 150 °C in a sealed tube for 12 h, a 75/25 mixture of the two perbutylated cyclopolystannanes **1** and **2**, respectively, was quantitatively produced, as determined by ¹H and ¹¹⁹Sn NMR spectroscopy and reverse-phase HPLC (Scheme 3).^{11,12} Following this thermolysis by ¹H NMR (sealed tube, benzene-*d*₆) revealed that only ethylene and ethanol

Scheme 3



were being produced alongside the formation of the cyclopolystannane products, thereby suggesting that the formal overall two-step process shown in Scheme 1 is indeed being realized. No trace of the proposed intermediate dibutylethoxystannane [Bu₂SnH(OEt)] was detected, however, and this supports the expectation that, if formed, compounds of this type are thermally unstable at the temperatures employed. Interestingly, it was observed that while the ratio of **1** to **2** varied from one thermolysis run to another, the cyclopentastannane **1** in the product always predominates. Finally, heating a solution of either a mixture of **1** and **2** or a pure sample of the cyclohexastannane **2** in benzene-*d*₆ (sealed tube) at 150 °C for 3 days led to neither decomposition nor interconversion of the two cyclopolystannanes, as determined by ¹¹⁹Sn NMR spectroscopy. This last observation suggests that the initially obtained product ratio is a kinetic one and that the barriers to Sn–Sn bond dissociation in these compounds are sufficiently high to prevent interconversion of the two.¹³

Establishing the detailed mechanism by which the cyclopolystannanes **1** and **2** are produced from **4** is of interest with respect to the further utilization of this potential new thermal route to cyclopolystannanes. Accordingly, it was important to discover that, under identical conditions, the solution thermolysis of tributylstannane (150 °C) generated only hexabutyldistannane, with no trace of **1** or **2** being observed. While this result supports the involvement of a β-elimination process in the thermolysis of **4**, it was somewhat surprising to find that (2-ethoxyethyl)tributylstannane (**6**), prepared from the hydrostannation of ethyl vinyl ether by tributylstannane,¹⁴ did not undergo β-elimination at 150 °C in solution to produce ethoxytributylstannane, as expected, but instead remained unchanged. This latter result suggests that the thermal β-elimination of the 2-ethoxyethyl substituent in **4** is likely occurring in a syn fashion via a cyclic transition state^{6a} rather than through either an anti β-elimination mechanism^{3b} or through simple Sn–C bond homolysis. As a further probe of the mechanism, the thermolysis of **4** was conducted in the presence of 10 equiv of norbornadiene, and as revealed in Scheme 3, this

(7) Sita, L. R.; Terry, K. W.; Shibata, K. *J. Am. Chem. Soc.* **1995**, *117*, 8049.

(8) Sita, L. R. *Organometallics* **1992**, *12*, 1442.

(9) Preparation of bis(2-ethoxyethyl)dibutylstannane (**5**): In a thick-walled Schlenk flask equipped with a Kontes Teflon valve was placed 2.9 g (8.08 mmol) of dibutylstannane, 10 mL of ethyl vinyl ether, and 10 mg of 2,2'-azobis(2-methylpropionitrile) (AIBN). The flask was then sealed and heated to 65 °C for 26 h, after which time the volatiles were removed *in vacuo* and the remaining colorless material bulb-to-bulb distilled (95 °C, 40 mmHg) to yield 2.74 g of pure **5** (90% yield). For **5**: ¹H NMR (benzene-*d*₆) δ 0.96–1.01 (multiplet, 10 H), 1.13 (t, 6 H, *J* = 6.9 Hz), 1.29 (t, 4 H, *J* = 7.5 Hz), 1.39 (sext, 4 H, *J* = 7.5 Hz), 1.56–1.66 (multiplet, 4 H), 3.30 (q, 4 H, *J* = 6.9 Hz), 3.61 (t, 4 H, *J* = 7.5 Hz); ¹³C{¹H} NMR (benzene-*d*₆) δ 10.16, 11.99, 14.01, 15.65, 27.84, 29.66, 65.63, 69.47; ¹¹⁹Sn{¹H} NMR (benzene-*d*₆) δ –17. Anal. Calcd for C₁₆H₃₆O₂Sn: C, 50.69; H, 9.19. Found: C, 50.25; H, 9.61.

(10) Preparation of dibutyl(2-ethoxyethyl)stannane (**4**): To a solution of 5.95 g (15.7 mmol) of **5** in 400 mL of deoiled pentane, cooled to –78 °C, was slowly added a solution of 2.23 g (15.7 mmol) of DIBAL-H in 45 mL of pentane dropwise over a period of 1 h. The mixture was then slowly warmed to room temperature and stirred overnight (~16 h), whereupon it was cooled to 0 °C and 1 mL of degassed water slowly added via a syringe. After removal of the cooling bath, the reaction mixture was stirred for 45 min; an excess of anhydrous sodium sulfate was then added, and stirring was continued. The mixture was then gravity-filtered through a glass frit containing a 1 in. × 3 in. pad of sodium sulfate. The volatiles were removed from the filtrate *in vacuo*, and the product was bulb-to-bulb-distilled (75–80 °C, 20 mmHg) to provide 4.02 g of pure **4** as a colorless oil (87% yield). For **4**: ¹H NMR (benzene-*d*₆) δ 0.92 (t, 6H, *J* = 7.2 Hz), 0.95–1.02 (multiplet, 4 H), 1.10 (t, 3 H, *J* = 6.9 Hz), 1.285 (td, 2 H, *J* = 7.2 Hz, *J* = 1.8 Hz), 1.36 (sext, 4 H, *J* = 7.2 Hz), 1.53–1.64 (multiplet, 4 H), 3.26 (q, 2 H, *J* = 6.9 Hz), 3.54 (t, 2 H, *J* = 7.5 Hz), 5.11 (sept, 1 H, *J* = 1.8 Hz); ¹³C NMR (benzene-*d*₆) δ 8.99, 10.84, 13.92, 15.53, 27.47, 30.25, 65.68, 69.43; ¹¹⁹Sn NMR (benzene-*d*₆) δ –95; IR (neat; cm^{–1}) 1810 s (ν_{SnH}). Anal. Calcd for C₁₂H₂₈O₂Sn: C, 46.94; H, 9.19. Found: C, 47.27; H, 9.60.

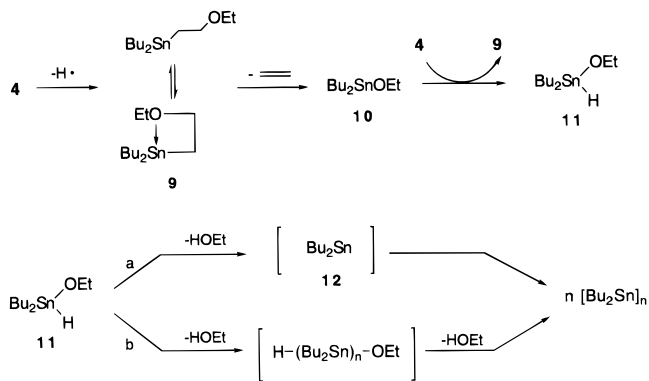
(11) Compounds **1** and **2** were identified on the basis of their ¹¹⁹Sn NMR spectral parameters, which are identical with those previously reported for these cyclopolystannanes.¹ In addition, a pure sample of **2** was obtained by preparative reverse-phase HPLC (acetonitrile/dichloromethane gradient).

(12) Compound **1** is much more sensitive (reactive) than **2**, and thus, in our hands, all purification procedures, including analysis by HPLC, tend to shift the product ratio in favor of the latter. Accordingly, ratios were obtained from integrated inverse gated-decoupled ¹¹⁹Sn NMR spectra of the initially obtained thermolysis product.

(13) As noted previously by Jousseau et al.,¹ this thermal stability of **1** and **2** is in stark contrast to that displayed by dodecamethylcyclohexastannane; see: Watta, B.; Neumann, W. P.; Sauer, J. *Organometallics* **1985**, *4*, 1954.

(14) For **6**: Anal. Calcd for C₁₆H₃₆O₂Sn: C, 52.92; H, 9.99. Found: C, 52.98; H, 10.27.

Scheme 4



resulted in the formation of an inseparable mixture of products, **7** and **8** (88/12, respectively; 87% isolated yield after chromatography), that are expected for a monohydrostannation of this reactive diene that occurs through a radical process.¹⁵ Here, it is important to note that no trace of the cyclopolystannanes **1** and **2** was observed, and by using the radical initiator AIBN, an identical result could be obtained at the lower temperature of 90 °C. Finally, when 10 equiv of the less reactive diene, 1,5-cyclooctadiene, was employed at 150 °C, a complex mixture of hydrostannated products and the cyclopolystannanes **1** and **2** was now obtained.

Together, the above results indicate that, as shown in Scheme 4, the first step in the thermolysis of **4** is loss of a hydrogen atom to generate the trivalent tin complex **9**. This intermediate has only a limited lifetime before undergoing a β-elimination that may be facilitated by both the electron-deficient character and decreased steric environment of the tin center that permits formation of the four-centered transition state. The product **10** of this β-elimination might then abstract a hydrogen atom from **4** to establish a radical-chain process that produces the thermally unstable intermediate Bu₂SnH(OEt) (**11**). Whether **11** undergoes con-

(15) Similar product mixtures are obtained from the radical initiated monohydrostannation of norbornadiene with trialkylstannanes; see: (a) Kuivila, H. G. *Acc. Chem. Res.* **1968**, *1*, 299. (b) Peterson, D. J.; Robbins, M. D.; Hansen, J. R. *J. Organomet. Chem.* **1974**, *73*, 237.

certed loss of ethanol to produce the divalent tin species **12** that then rapidly cyclopolymers (route a),¹⁶ or whether the cyclopolystannanes **1** and **2** are obtained from the ring closing of α,ω-difunctional linear polystannane oligomers that are built up from a series of intermediate hydrostannolysis reactions¹⁷ (route b), is still not clear at the present time. It is important to point out, however, that no trace of tin hydride intermediates are ever observed by ¹H NMR spectroscopy during, or after, thermolysis of **4**. In contrast, these tin hydride intermediates are clearly seen during the room-temperature cocondensation reaction between **3** and Bu₂Sn(OMe)₂ that was mentioned previously.⁵ Unfortunately, it has not yet been possible to identify a reagent that can serve to effectively trap the proposed stannylene intermediate **12**,¹⁸ and thus the exact pathway leading to the cyclopolystannanes **1** and **2** remains open to further investigation.

In conclusion, we have presented the initial demonstration of a new route to cyclopolystannanes that proceeds through a formal overall reductive-elimination pathway.¹⁹ In addition, this route apparently involves the first documented instance of a β-elimination reaction occurring for a trivalent tin species. Efforts are currently in progress to extend these studies to the thermal generation of other cyclopolystannane systems, as well as to further elucidate the mechanism by which this novel transformation occurs.

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(16) A mechanism similar to this has been previously proposed for the decomposition of compounds of the general formula R₂MH(OMe) (M = Ge and Sn); see ref 4 and: Massol, M.; Satgé, J.; Rivière, P.; Barrau, J. *J. Organomet. Chem.* **1970**, *22*, 599.

(17) Neumann, W. P. *The Organic Chemistry of Tin*; Wiley: New York, 1970.

(18) For instance, attempts to trap **12** with 2,3-dimethylbutadiene led only to a complex mixture of hydrostannated products resulting from trapping of the intermediate **9**.

(19) Cyclopolystannanes formally possess Sn(II) centers.