Straightforward Preparation of Unsymmetrical Triorganotin Hydrides through New (Diorganostannyl)lithiums

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Received October 7, 1993®

Summary: Metalation of diorganostannanes $R^1_2SnH_2$ by lithium diisopropylamide afforded the corresponding (diorganostannyl)lithiums, R^1_2SnHLi. Further reaction with halides led to unsymmetrically substituted alkyldiorganostannanes, $R^1_2R^2SnH$. In situ stepwise dimetalation of diorganostannanes $R^1_2SnH_2$ gave the expected dialkylation products $R^1_2R^2_2Sn$ with organic halides, aldehydes, and epoxides.

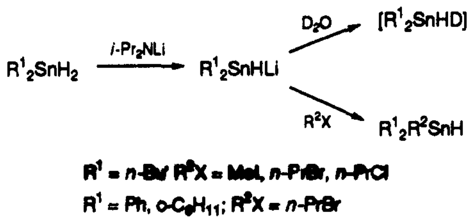
Triorganostannanes are usually obtained via the reaction of organotin oxides, alkoxides, or halides with reducing agents such as silicon, aluminum, or boron hydrides.[1] This reaction is straightforward for the preparation of triorganostannanes with three identical organic groups. The synthesis of unsymmetrical triorganostannanes, however, requires a long and tedious multistep route, as the monoalkylation of dihalodiorganostannanes is usually not selective:[2]

$$R^1_2SnX_2 \rightarrow R^1_2SnPh_2 \rightarrow R^1_2PhSnX \rightarrow R^1_2PhSnR^2 \rightarrow R^1_2R^2SnX \rightarrow R^1_2R^2SnH$$

A very simple and direct way to prepare unsymmetrical triorganostannanes could be the alkylation of (diorganostannyl)lithiums R^1_2SnHLi by organic halides, (organostannyl)lithiums being in general easy to alkylate.[3] We thus studied the metalation of diorganostannanes and the subsequent alkylation of the stannyllithium intermediates.

Treatment of a THF–hexane solution of lithium diisopropylamide[4] with an equimolar amount of dibutylstannane at low temperature, followed by the addition of deuterium oxide, afforded deuteriodibutylstannane[5] in 70% yield (>95% D). Thus, the existence of a new stannyllithium, (dibutylstannyl)lithium (Bu_2SnHLi), was established.[6] Replacement of deuterium oxide by iodomethane gave the desired methyldibutylstannane[9] in 45% yield, showing that the creation of a new tin–carbon bond is possible in this way. The alkylation was not limited to iodides, as bromides and chlorides could be used as well. 1-Bromopropane gave the corresponding stannane in 60% yield. 1-Chloropropane led to *n*-propyldibutylstannane in 57% yield.[10] This new reagent, (dibutylstannyl)lithium, is particularly interesting for the grafting of tin–hydride units on halogenated polymers in only one step, in order to prepare tin–hydride-supported reagents.[12] Known preparations require a multistep procedure.[13] Dibutylstannane was not the only diorganostannane able to be monometalated; the reaction was general enough to be successfully extended to diphenyl- and dicyclohexylstannanes. Lithiation of diphenyl- and dicyclohexylstannanes followed by alkylation with 1-bromopropane led to the corresponding propyldiphenyl- and propyldicyclohexylstannanes in 50 and 63% yield, respectively (Scheme 1).

Scheme 1



R^1 = *n*-Bu; R^2X = MeI, *n*-PrBr, *n*-PrCl
R^1 = Ph, c-C_6H_{11}; R^2X = *n*-PrBr

A few disodium[14] and dilithium[15] derivatives of diorganostannanes are known. They are prepared through treatment of a dihalodiorganostannane with a metal, which

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● Abstract published in *Advance ACS Abstracts,* December 1, 1993.

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(5) This compound appears as a statistical mixture of Bu_2SnH_2, Bu_2SnHD, and Bu_2SnD_2.

(6) The preparation of a much more complicated reagent of the same type, [(2,4,6-tris(bis(trimethylsilyl)methyl)phenyl)(2,4,6-triisopropylphenyl)stannyl]lithium, obtained by the metalation of the corresponding dihydride by *tert*-butyllithium, has been very recently[7] independently[8] reported.[7,8]

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(10) In a typical procedure, 5.17 g (22 mmol) of dibutylstannane[11] was slowly added to a THF (20 mL)–hexane (8 mL) solution of lithium diisopropylamide (20 mmol) at −70 °C under nitrogen. After 30 min at −50 °C the solution was golden yellow. Then, 1.56 g (20 mmol) of 1-chloropropane was added, and the mixture was warmed to 0 °C. After hydrolysis and the usual workup, propyldibutylstannane (57%) was purified by distillation (Kugelrohr apparatus, oven temperature 110 °C, 10^{-4} mmHg). *n*-Propyldibutylstannane: ^1H NMR δ 0.9 (m, 15H), 1.30 (m, 4H), 1.55 (m, 6H), 5.02 (m, 1H); ^{13}C NMR δ 8.5, 11.2, 13.7, 18.4, 21.3, 27.9, 30.3; ^{119}Sn NMR δ −89. Anal. Calcd for $C_{11}H_{26}Sn$: C, 47.69; H, 9.46. Found: C, 47.12; H, 9.14. *n*-Propyldiphenylstannane: ^1H NMR δ 0.90 (t, 3H), 1.21 (t, 2H), 1.62 (m, 2H), 6.34 (m, 1H), 7.19 (m, 10H); ^{13}C NMR δ 13.1, 18.3, 20.8, 128.8, 129.1, 129.2, 137.5; ^{119}Sn NMR δ −137. Anal. Calcd for $C_{15}H_{18}Sn$: C, 56.83; H, 5.72. Found: C, 56.38; H, 5.27. *n*-Propyldicyclohexylstannane: ^1H NMR δ 0.93 (m, 2H), 1.02 (t, 3H), 1.25–1.90 (m, 24H), 5.15 (s, 1H); ^{13}C NMR δ 10.0, 19.2, 21.8, 25.8, 27.4, 29.2, 33.2 (1C), 33.3 (1C); ^{119}Sn NMR δ −87.9. Anal. Calcd for $C_{15}H_{30}Sn$: C, 54.75; H, 9.19. Found: C, 54.98; H, 8.95.

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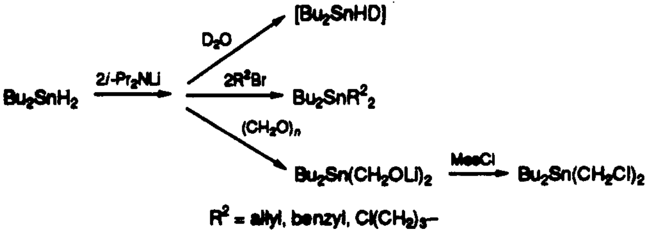
(12) Ruel, G. Thesis, Bordeaux, France, 1993.

(13) Weinshenker, N. M.; Crosby, G. A.; Wong, J. Y. *J. Org. Chem.* 1975, *40*, 1966. Ueno, Y.; Moriya, O.; Chino, K.; Watanabe, M.; Okawara, M. *J. Chem. Soc., Perkin Trans.* 1986, 1351. Miller, B. L.; Hershberger, J. W. *J. Polym. Sci., Part C* 1987, *25*, 219. Neumann, W. P. *J. Organomet. Chem.* 1992, *437*, 23. Ruel, G.; Ke The, N.; Dumartin, G.; Delmond, B.; Pereyre, M. *J. Organomet. Chem.* 1992, *444*, C18.

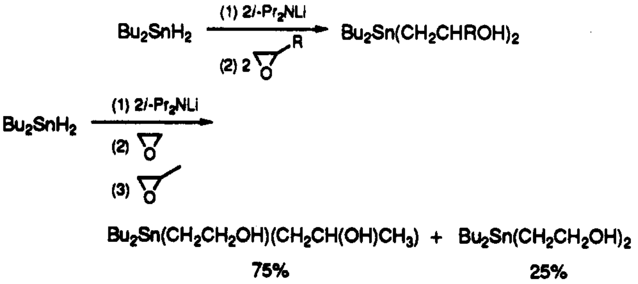
0276-7333/94/2313-0024$04.50/0

involves intermediates with tin–tin bonds and their cleavage by the metal. As the stability of these dimetalated intermediates was established, dimetalation of diorganostannanes with 2 equiv of lithium diisopropylamide was attempted, to give an alternative route to $R^1_2SnLi_2$. Unfortunately, quenching with deuterium oxide only afforded deuteriodibutylstannane in 81% yield, indicating that dimetalation did not occur. However, two successive *in situ* metalations can successfully be performed when 2 equiv of lithium diisopropylamide and dibutylstannane are mixed together, followed by alkylating agents such as organic halides. Bis(2-propenyl)dibutylstannane[16] (75%), bis(phenylmethyl)dibutylstannane[17] (45%), and bis(3-chloropropyl)dibutylstannane[18] (47%) could be prepared in this way. This procedure is well-suited for the preparation of such dihalogenated tetraorganostannanes, as three steps were necessary to obtain bis(3-chloropropyl)dimethylstannane[19] in low yield from dimethylstannane (overall yield 7%), the final chlorination step being particularly inefficient. With 1,3,5-trioxane or epoxides,[20] the desired coupling compounds were also obtained. With 1,3,5-trioxane, the stannylated diol was transformed *in situ* into the corresponding chloride[21] by mesyl chloride[22] (40% yield) for easier characterization (Scheme 2).

Scheme 2



Scheme 3



The reaction of epoxides was particularly interesting, as it gave an easy entry into thermally labile bis(2-hydroxyethyl)dialkylstannanes[23] (R = H, 60% yield; R = Me, 51% yield) showing latency properties[24] in the catalysis of silicone curing and polyurethane preparation (Scheme 3). Furthermore, the reaction can be used to prepare unsymmetrical diols, as successive addition of two different epoxides led to the corresponding unsymmetrical diol (45% yield), contaminated with 25% of the symmetrical diol from the first epoxide.

Acknowledgment. We are indebted to Rhône-Poulenc Co. for financial support and to Shering-France and Sipcam-Phyteurop for a generous gift of chemicals.

OM930693A

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(18) Bis(3-chloropropyl)dibutylstannane: ^1H NMR δ 0.9 (m, 7H), 1.15 (m, 2H), 1.45 (m, 2H), 1.90 (m, 2H), 3.3 (t, 4H); ^{13}C NMR δ 6.0, 8.8, 13.7, 27.8, 29.3, 30.4, 48.2; ^{119}Sn NMR δ −137. Anal. Calcd for $C_{14}H_{30}Cl_2Sn$: C, 43.34; H, 7.79. Found: C, 42.76; H, 7.41.

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(20) Dibutylstannane (4.7 g, 20 mmol) was slowly added to a THF (10 mL)–hexane (16 mL) solution of lithium diisopropylamide (42 mmol) at −50 °C. After 30 min at this temperature, the solution was golden yellow. Then, 2.2 g (50 mmol) of epoxide was added, and the mixture was warmed to 0 °C. After hydrolysis and the usual workup, the diol was recovered in 60% yield as an oil by chromatography on Florisil (eluant petroleum ether followed by diethyl ether). Bis(2-hydroxyethyl)dibutylstannane: ^1H NMR δ 0.9 (m, 10H), 1.10 (m, 4H), 1.25 (m, 4H), 1.45 (m, 4H), 3.7 (m, 4H), 4.20 (bs, 2H); ^{13}C NMR δ 9.8, 13.9, 14.5, 27.6, 29.4, 61.3; ^{119}Sn NMR δ −22.0. Anal. Calcd for $C_{12}H_{28}O_2Sn$: C, 44.62; H, 8.74. Found: C, 44.19; H, 9.12. Bis(2-hydroxypropyl)dibutylstannane: ^1H NMR δ 0.9 (m, 10H), 1.10 (d, 6H), 1.15 (m, 8H), 1.45 (m, 4H), 4.1 (m, 2H), 4.40 (bs, 2H); ^{13}C NMR δ 10.1, 13.7, 22.1, 27.4, 27.5, 29.2, 67.2; ^{119}Sn NMR δ −28.3 (0.5Sn), −28.8 (0.5Sn). Anal. Calcd for $C_{14}H_{32}O_2Sn$: C, 48.09; H, 9.19. Found: C, 48.47; H, 9.43. To 20 mmol of (dibutylstannyl)lithium at −50 °C was added 0.9 g (20 mmol) of ethylene oxide, and the mixture was warmed to −20 °C. After the temperature was lowered −50 °C, 1.2 g (20 mmol) of propylene oxide was added, and the mixture was warmed to 0 °C. After hydrolysis and the usual workup, the diol was recovered by liquid chromatography as above, contaminated by 25% of bis(2-hydroxyethyl)-dibutylstannane. (2-Hydroxyethyl)(2-hydroxypropyl)dibutylstannane: ^1H NMR δ 0.9 (m, 10H), 1.1–1.5 (m, 15H), 3.8 (m, 2H), 3.95 (bs, 2H), 4.1 (m, 1H); ^{13}C NMR δ 9.8, 13.6, 14.3, 21.8, 27.3, 27.6, 29.5, 61.4, 67.6; ^{119}Sn NMR δ −25.7.

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