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The preparation of a series of 1,ω-bis(hydridodimethylstannyl)alkanes $HSnMe_2(CH_2)_nSnMe_2H$ with $n = 1–6$ is described; spectroscopic data for the ditin dihydrides are provided.

Introduction

The most common method of preparation of triorganotin hydrides involves the use of a strong reducing agent, such as $LiAlH_4$[1] or DIBAL.[2] However, for more sensitive organotin hydrides, this method can be too harsh, and often results in polymerization of the reaction mixture and poor yields.

A second method preparation involves an exchange reaction between the organotin halide, R_3SnX, corresponding to the desired product, and a molecule of an easily prepared organotin hydride, R'_3SnH.

$$R_3SnX + R'_3SnH \rightleftharpoons R_3SnH + R'_3SnX$$

$$X = Cl, Br \qquad R' = Bu, Ph$$

As this is an equilibrium, either R'_3SnX must be easily removed or, more commonly, the desired hydride must be the lowest boiling fraction in the reaction mixture.

This second method has now been found to be useful in the preparation of 1,ω-bis(hydridodimethylstannyl)alkanes, $HMe_2Sn(CH_2)_nSnMe_2H$, from the corresponding bis(bromodimethylstannyl)alkanes. As the bis(bromodimethylstannyl)alkanes are well-known and simple to prepare,[3] this gives an easy synthetic route to a series of compounds that are otherwise difficult to obtain; only one dihydride of this type has so far been reported in the literature.[4]

Results and Discussion

The preparation of the bis(hydridodimethylstannyl)alkanes, $HMe_2Sn(CH_2)_nSnMe_2H$, is a three-step synthesis. The first two steps (the conversion of an α,ω-dihaloalkane, $X(CH_2)_nX$ (X = Cl, Br), into the bis(trimethylstannyl)alkane, $Me_3Sn(CH_2)_nSnMe_3$, and the subsequent bromodemethylation using dimethyltin dibromide in a 2:1 molar ratio to give the corresponding bis(bromodimethylstannyl)alkane) have already been described in the literature.[3]

The bis(hydridodimethylstannyl)alkanes were prepared from the dibromides by using both $LiAlH_4$/DIBAL and R'_3SnH. As can be seen from the results summarized in Table I, the exchange reaction with a second tin hydride gave better overall yields, when compared to the equivalent reaction using an aluminium hydride. In addition, the purification of the product is much simpler when the tin hydride equilibrium is employed. As opposed to the typical aqueous workup, where the reaction mixture is prone to decomposition and polymerization, the exchange reaction allows for immediate distillation of the product from the reaction mixture.

When tributyltin hydride is used in a 2:1 molar ratio of Bu_3SnH to $BrMe_2Sn(CH_2)_nSnMe_2Br$ (Table I, entries 1–3), the equilibrium appears to be shifted approximately 50% to the right-hand side, as shown by ^1H NMR spectroscopy (integration of the $BrMe_2Sn–$ singlet versus the $HMe_2Sn–$ doublet).

Table I. Preparation of Bis(hydridodimethylstannyl)alkanes

compd $HMe_2Sn(CH_2)_nSnMe_2H$	method of prepn	yield, %	bp, °C/mmHg
$n = 1$ (1)	DIBAL	53	
	Bu_3SnH^a	80	65–68/12
$n = 2$ (2)	DIBAL	40	
	Bu_3SnH^a	74	46–48/1.0
$n = 3$ (3)	Bu_3SnH^a	47	56–59/1.5
$n = 4$ (4)	$LiAlH_4$	48[c]	
	Ph_3SnH^b	60	67–69/0.55
$n = 5$ (5)	$LiAlH_4$	0	
	Ph_3SnH^b	45	57–60/0.03
	$PS–C_2H_4–SnBu_2H^d$	18	
$n = 6$ (6)	$LiAlH_4$	12	
	Ph_3SnH^b	53	128–135/0.6

[a] Reaction time, 1.5 h at 50–65 °C. [b] Reaction time, 3 h at 40 °C. [c] Lit.[4] 60%. [d] PS = polystyrene, benzene used as solvent; reaction time, 4 days at 45 °C.

While complete conversion can be achieved by using Bu_3SnH in a 4:1 molar ratio, this does not increase the overall yield, as removal of the product from the reaction mixture also causes the system to shift its equilibrium favorably.

Because the equilibrium does not provide complete reaction, yields were highest when the distillation of the product was carried out slowly with the lowest temperature/highest vacuum combination possible, using 2 equiv of tributyltin hydride/mol of ditin dibromide. Alternatively, the product may be removed by using a dynamic vacuum system; the reaction mixture is subject to reduced pressure, corresponding to evolution of the bis(hydridodimethylstannyl)alkane, and collected in a flask cooled by liquid nitrogen (this is a modification of the procedure used by Kuivila in the preparation of Me_2SnH_2).[5]

For all of the products prepared by using Bu_3SnH, a second distillation was carried out to obtain a high degree of purity. This is especially important for 1,3-bis(hydridodimethylstannyl)propane, where the boiling point of the product approaches that of Bu_3SnH. Although separation is somewhat difficult, the product can be purified by distillation when both the temperature and vacuum are controlled carefully.

Because of the similarity of the boiling points of 1,3-bis(hydridodimethylstannyl)propane and tributyltin hydride, it was decided that another organotin hydride would have to be used in the exchange reaction if the alkyl chain were lengthened further. In order to allow for a large difference in boiling points, Ph_3SnH was chosen. Although not ideal, due to thermal instability, it is easy to prepare from Ph_3SnCl[6] and allows for easy removal of the product

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Table II. ^{1}H NMR Data for Compounds 1–6[a]

compd	δ(Me$_2$Sn)	δ(Sn*H*)	δ(C*H*$_2$)[b]
1[c]	0.18 [d, ^3J(HH) = 2.1] ^2J(SnH) = 56	4.90 (m) ^1J(SnH) = 1752	–0.15 (t) ^2J(SnH) = 60
2[d]	0.10 [d, ^3J(HH) = 2.1] ^2J(SnH) = 53	4.80 (m) ^1J(SnH) = 1688	1.12 (s) ^3J(SnH) = 84
3	0.11 [d, ^3J(HH) = 2.3] ^2J(SnH) = 54	4.86 (m) ^1J(SnH) = 1686	0.91 (m, α) 1.72 (m, β) ^2J(SnH) = 57
4	0.15 [d, ^3J(HH) = 2.3] ^2J(SnH) = 54	4.90 (m) ^1J(SnH) = 1683	0.9 (m, α) 1.54 (m, β) ^2J(SnH) = 55
5	0.16 [d, ^3J(HH) = 2.4] ^2J(SnH) = 53	4.93 (m) ^1J(SnH) = 1679	0.93 (m, α) 1.38 (m, β) ^2J(SnH) = 54 1.56 (m, γ)
6	0.15 [d, ^3J(HH) = 2.4] ^2J(SnH) = 53	4.91 (m) ^1J(SnH) = 1680	0.91 (m, α) 1.34 (m, β) ^2J(SnH) = 55 1.55 (m, γ)

[a] Chemical shifts in ppm with respect to TMS; coupling constants (to ^{119}Sn) in Hz. [b] α, β, and γ refer to the position of the methylene groups with respect to the stannyl moieties. [c] Values consistent with those reported by Fabisch.[8] [d] Values consistent with those reported by Faust.[9]

from the reaction mixture. As is the case with Bu_3SnH, Ph_3SnH gives better yields when compared to the procedure using $LiAlH_4$ (Table I, entries 4–6). For compounds **5** and **6**, the use of $LiAlH_4$ proved extremely difficult and gave very poor yields.

In the reactions employing triphenyltin hydride, a 2:1 molar ratio of Ph_3SnH to $BrMe_2Sn(CH_2)_nSnMe_2Br$ caused the reaction to go to approximately 10% completion, as measured from the ^{1}H NMR spectra. Again, this can be overcome by using an excess of Ph_3SnH. It is however more efficient to remove the product, allow the system to reattain equilibrium, and continue in this manner until ^{1}H NMR analysis shows no further ditin dibromide to be present. This process is facilitated by the use of Ph_3SnH, as the other components of the system have much higher boiling points than the required ditin dihydride.

A further method of preparation tried used a polymer-supported organotin hydride[7] (Table I, entry **5**). Initially, this system appears more efficient than Ph_3SnH, as mixing of the starting materials in a 2:1 molar ratio of adducts resulted in 25% conversion to product, as shown by ^{1}H NMR spectroscopy. However, as a solvent must be used in this system, the reaction is halted upon removal of the latter. This, in turn, does not permit the use of the dynamic system mentioned above. This problem can be overcome by using an excess of the polymer-supported organotin hydride or by readding solvent to the system to allow equilibrium to be reestablished.

NMR Data. The ^{1}H NMR data, presented in Table II, show very consistent values for all chemical shifts and coupling constants. The only coupling value that shows a large amount of variation is ^3J(SnH), which will be dependent upon the dihedral bond angles adopted by each particular molecule. This coupling could not be resolved in the larger molecules.

The chemical shifts of the methylene groups are also prone to variation, as would be expected from the different chemical environments in which they are found. However, upon lengthening the alkyl chain separating the two tin moieties, the shift values converge. It is interesting to note that the methylene group in compound **1** resonates upfield from the methyl groups. There is a dramatic shift for compound **2**, where the resonance is found at 1.1 ppm. However, upon extending the alkyl chain to $-(CH_2)_3-$, the shielding effect of the tin is diminished, and the chemical shifts differ only slightly in compounds **3–6**.

Table III. ^{13}C and ^{119}Sn NMR Data for Compounds 1–6[a]

compd	δ(*Me*$_2$Sn)	δ(*C*H$_2$)[b]	δ(^{119}Sn)
1[c]	−10.2 [346.0]	−19.8 [285]	−77.1 [305]
2	−12.6 [329.6]	−6.5 [366.2, 35.6]	−94.8 [1141]
3	−12.5 [330.9]	14.6 [371.8, 61.0], α 25.7 [20.9], β	−104.7
4	−12.4 [330.6]	9.2 [376.3], α 31.8 [20.6, 58.5], β	−100.4
5	−12.5 [330.6]	9.6 [378.9], α 27.2 [22.9], β 38.5 [53.4], γ	−100.3
6	−12.5 [328.0]	9.7 [379.0], α 27.6 [21.6], β 33.9 [55.9], γ	

[a] Chemical shifts in ppm with respect to TMS or Me_4Sn, respectively; coupling constants (in brackets) in Hz (coupling to ^{119}Sn reported). [b] α, β, and γ refer to the positions of the methylene groups with respect to the tin moieties. [c] Values are consistent with those reported by Fabisch.[8]

The ^{13}C NMR data, presented in Table III, show the same patterns as seen in the ^{1}H NMR data. Due to the similarities of the compounds reported here, the parameters vary little within the series of compounds, as expected. Just as in the ^{1}H NMR data, the greatest change is seen in the methylene group chemical shifts, the values of which change dramatically between compounds **1** and **2**; there is little change upon further lengthening the alkyl chain.

While the ^{119}Sn NMR shifts vary considerably between compounds **1** and **2**, the values for **3–6** are very similar. The coupling constants reported here are of the expected magnitude and are comparable to those from related systems. Tin–tin coupling could not be detected across more than three bonds.

Experimental Section

All manipulations involving organotin compounds were carried out under argon. Routine proton NMR spectra were recorded by using a Varian EM-360 instrument and high-resolution NMR spectra by using a Bruker AM-300 spectrometer. IR spectra were obtained by using a Perkin-Elmer 577 instrument, mass spectra, with a Finnigan MAT 8230 spectrometer.

Preparation of Bis(hydridodimethylstannyl)alkanes. Method A (DIBAL). To a solution of 2.1 molar equiv of DIBAL in Et_2O, cooled to −75 °C, was added dropwise a 1.0 molar equiv solution of bis(bromodimethylstannyl)alkane in Et_2O. Upon completion of the addition, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. All volatile components were removed from the reaction mixture under reduced pressure. Ether was then distilled off and the dihydride distilled under reduced pressure. This method was used for the preparation of $HMe_2SnCH_2SnMe_2H$ and $HMe_2Sn(CH_2)_2SnMe_2H$.[7]

Method B ($LiAlH_4$). To a suspension of 2.1 molar equiv of $LiAlH_4$ in Et_2O was added dropwise a 1.0 molar equiv solution of bis(bromodimethylstannyl)alkane in THF/Et_2O (3:2 v/v). Upon completion of the addition, the reaction mixture was heated to reflux for 1 h. After cooling, water was added dropwise to quench the reaction. After filtration, solvents were removed under reduced pressure. Fine distillation under reduced pressure provided the product in high purity. This method is recommended for the preparation of $HMe_2Sn(CH_2)_4SnMe_2H$ and $HMe_2Sn(CH_2)_6SnMe_2H$.

Method C (R_3SnH). A 2 molar equiv sample of Bu_3SnH and 1 molar equiv of $BrMe_2Sn(CH_2)_nSnMe_2Br$, n = 1–3, were mixed and stirred under argon at 50–65 °C. The reaction was followed by the appearance of a doublet in the ^{1}H NMR spectrum due to the methyl groups of the Me_2SnH moiety. In general, the reactions

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were allowed to run for 1.5 h, at which time the desired product was removed under reduced pressure. The system was allowed to reattain equilibrium, and the process was repeated. For all compounds, a second distillation was performed to ensure product purity.

When Ph_3SnH was used in the exchange reaction, $n = 4$–6, the temperature of the reaction mixture was lowered to 45 °C due to the thermal instability of Ph_3SnH. The reaction time was also increased to 2 h, after which the product was removed under reduced pressure, as reported above.

Using this method, with either Bu_3SnH or Ph_3SnH, provided all of the dihydrides discussed here.

The polymer-supported organotin hydride (10.1 g, 0.95 mmol of SnH/g of polymer) was treated with benzene (25 mL) and $BrMe_2Sn(CH_2)_5SnMe_2Br$ (2.5 g, 4.7 mmol). After the reaction mixture was shaken under argon for a period of 4 days at 50 °C, benzene and product were removed under reduced pressure. Removal of the benzene gave the desired product (0.33 g, 19%) in high purity. It should be noted that the reaction reaches equilibrium fairly quickly and that the yield is not improved by the use of longer reaction times.

Infrared and mass spectroscopic data and C, H analysis values for the ditin dihydrides are reported below.

1,1-Bis(hydridodimethylstannyl)methane (1): IR ν_{Sn-H} 1823 cm^{-1}; MS 313 (M^+ - H, 50%), 297 (M^+ - (Me + 2H), 33.9%), 283 (M^+ - 2Me, 39.4%), 150 ($SnMe_2$, 8.3%), 135 (SnMe, 64.7%). Anal. Calcd for $C_5H_{16}Sn_2$: C, 19.1; H 5.1. Found: C, 18.9; H, 4.8.

1,2-Bis(hydridodimethylstannyl)ethane (2): IR ν_{Sn-H} 1813 cm^{-1}; MS 328 (M^+, 2.1%), 299 (M^+ - 2Me, 11.8%), 135 (SnMe, 82.7%). Anal. Calcd for $C_6H_{18}Sn_2$: C, 22.2; H, 5.0. Found: C, 21.6; H, 5.4.

1,3-Bis(hydridodimethylstannyl)propane (3): Ir ν_{Sn-H} 1818 cm^{-1}; MS 341 (M^+ - H, 100%), 327 (M^+ - Me, 39.4%), 151 ($HSnMe_2$, 50%), 135 (SnMe, 75.7%). Anal. Calcd for $C_7H_{20}Sn_2$: C, 24.6; H 5.9. Found: C, 25.0; H, 5.8.

1,4-Bis(hydridodimethylstannyl)butane (4): IR ν_{Sn-H} 1820 cm^{-1}; MS 355 (M^+ - H, 100%), 191 (M^+ - ($H+CH_2SnMe_2H$), 78.9%), 151 ($HSnMe_2$, 22%), 135 (SnMe, 24%). Anal. Calcd for $C_8H_{22}Sn_2$: C, 27.0; H, 6.2. Found: C, 27.4; H, 6.1.

1,5-Bis(hydridodimethylstannyl)pentane (5): IR ν_{Sn-H} 1820 cm^{-1}; MS 369 (M^+ - H, 8.7%), 205 (M^+ - ($H+CH_2SnMe_2H$), 100%), 151 ($HSnMe_2$, 47%), 135 (SnMe, 93.6%). Anal. Calcd for $C_9H_{24}Sn_2$: C, 29.3; H, 6.5. Found: C, 29.7; H, 6.1.

1,6-Bis(hydridodimethylstannyl)hexane (6): IR ν_{Sn-H} 1822 cm^{-1}; MS 383 (M^+ - H, 100%), 219 (M^+ - ($H+CH_2SnMe_2H$), 45%), 151 ($HSnMe_2$, 22%), 135 (SnMe, 15%). Anal. Calcd for $C_{10}H_{26}Sn_2$: C, 31.3; H, 6.8. Found: C, 31.7; H, 6.9.

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Reaction of Stannyl-Substituted Phosphorus Ylides with Boron Trifluoride Diethyl Etherate: Evidence for Formation of Transient Triphenylphosphonio-Substituted Stannaethenes

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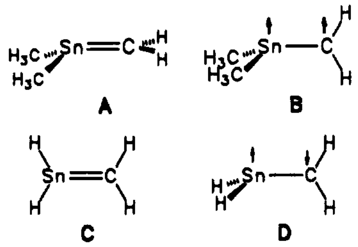
The reaction of the stannyl-substituted phosphorus ylide $Ph_3PCH(SntBu_2OiPr)$ (**4**) with boron trifluoride diethyl etherate yields [1,1,3,3-Tetra-*tert*-butyl-2,4-bis(triphenylphosphonio)-1,3-distannetane] bis(tetrafluoroborate) (**11**) in addition to $Ph_3PCH_2SntBu_2F^+BF_4^-$ (**12**) and boranyl-substituted phosphorus ylides (**13**). If the reaction is performed in the presence of benzophenone, (2,2-diphenylvinyl)triphenylphosphonium tetrafluoroborate (**15**) is isolated. The reactive intermediate in these experiments could be a triphenylphosphonio-substituted stannaethene (stannavinylphosphonium salt), $Ph_3PCH{=}SntBu_2{}^+BF_4^-$ (**14**), although reaction routes not involving a low-coordinate tin species are possible. A different reactivity is shown by the ylide $Ph_3PCCH_3(SntBu_2OiPr)$ (**5**), which reacts with boron trifluoride diethyl etherate with formation of a betaine, $Ph_3PCCH_3(BF_3)(SntBu_2F)$ (**22**). If benzophenone is added as trapping reagent, reduction to diphenylcarbinol, Ph_2CHOH, is observed and the vinylphosphonium salt $Ph_3P^+(C{=}CH_2)SntBu_2FBF_4^-$ (**23**) is isolated. This unusual reactivity is explained by a migration of a hydrogen atom from the methyl group in $Ph_3PCCH_3{=}SntBu_2{}^+BF_4^-$ (**21a**) to the low-coordinate tin center via a cyclic hydrogen-bridged intermediate with a three-center, 2-electron bond (**21c**). The reaction behavior of the assumed transient stannavinylphosphonium salts finds parallels in the well-known reactivity of silaethenes. The X-ray structures of the compounds $Ph_3PCH_2(SntBu_2F)^+BF_4^-$ (**12**), $Ph_3P(C{=}CH_2)SntBu_2F^+BF_4^-$ (**23**), and $[(Ph_3P)CHSntBu_2CH(PPh_3)SntBu_2{}^{2+}](BF_4^-)_2$ (**11**) are reported.

The chemistry of low-valent main-group element compounds that are isolobal with ethenes has focused on compounds incorporating either phosphorus, silicon, or germanium as the "heavy" atom.[1] In comparison, there is only limited information on such compounds of the heavier group 14 or 15 elements.[2] However, theoretical investigations carried out for stannaethenes support their existence. MNDO calculations performed by Dewar et al.[3] predict the orthogonal triplet biradical B to be 1.1 kcal

Chart I



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