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Reduction of dichlorodiphenylstannane

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Reduction of dichlorodiphenylstannane with lithium followed by treatment with methyl iodide gave methyltriphenylstannane, dimethyldiphenylstannane and 1,2-dimethyldistannane. 1,2-Dilithiodistannane and triphenylstannyllithium were intermediates of this reaction.

KEYWORDS: reduction; dichlorodiphenylstannane; 1,2-dilithiodistannane; triphenylstannyllithium

INTRODUCTION

1,1-Dilithium derivatives of the compounds containing a heavier Group 14 element are of interest from the viewpoint of structure, reactivity and as useful intermediates for the synthesis of compounds containing a heavier Group 14 element. Despite numerous reports on the synthesis of lithiometallanes (for monographs on organolithium chemistry, see Refs 1 and 2), less attention has been paid to acyclic 1,1-dilithiometallane because of synthetic difficulties Group 14 metallole dianions, cyclic 1,1-dilithium derivatives have been relatively well investigated owing to their unusual stability resulting from aromaticity.[3–11] Very recently, the silyl-substituted dilithiosilane[12–14] and dilithiogermane[15] have been reported as effective reagents for the preparation of doubly bonded compounds of heavier Group 14 elements. Aryl-substituted dilithiosilane[16–18] and dilithiogermane[19] have also been demonstrated as useful precursors for the synthesis of three-membered ring compounds. The generation of a dilithiostannane has been reported by the reduction of dichlorodiphenylstannane with lithium.[20] We have recently reported the 1,1-dilithiostannane having a cyclic structure with remarkable stability caused by delocalization of the negative charge into the five-membered ring.[21–23] In the course of our studies on 1,1-dilithiostannanes, we investigated the reduction of dichlorodiphenylstannane by lithium for the preparation of acyclic 1,1-dilithiostannanes and elucidation of their refined structures. We report herein the reaction of dichlorodiphenylstannane with lithium.

RESULTS AND DISCUSSION

Reaction of dichlorodiphenylstannane with excess lithium

Reaction of dichlorodiphenylstannane (**1**) with excess lithium in tetrahydrofuran (THF) was carried out according to the literature.[20] When a THF solution of dichlorodiphenylstannane was mixed with excess lithium at room temperature, the color of the reaction mixture turned to deep red, suggesting the formation of anionic species. Treatment of the mixture with excess methyl iodide gave methyltriphenylstannane (**2**; 13%), dimethyldiphenylstannane (**3**; 21%) and 1,2-dimethyldistannane (**4**; 12%) (Scheme 1). Removal of excess lithium from the reaction mixture followed by the treatment of the resulting solution with methyl iodide gave **4** (38%) as a major product, as well as **2** (9%) and **3** (4%). The formation of **3** can be explained in terms of methylation of the corresponding 1,1-dilithiostannane, and that of **4** similarly from the 1,2-dilithiodistannane. However, the formation of **2** was unexpected.

NMR study of the reduction of dichlorodiphenylstannane with lithium

To explore the intermediate leading to **2**, the reaction was monitored by NMR. The mixture of dichlorodiphenylstannane (**1**) and excess lithium in THF was placed in an NMR tube with C_6D_6 as NMR lock. The color of the solution changed to dark red. After allowing to stand for 5 min, the ^{119}Sn signal assignable to $(Ph_2Sn)_6$ (**5**) appeared at −208.6 ppm[24] as a main signal, with complete disappearance of the ^{119}Sn signal for **1** (−146.8 ppm). After several hours, two ^{119}Sn signals appeared, at −140.9 and −105.3 ppm. The signal at −105.3 ppm is assignable to triphenylstannyllithium (**6**; Scheme 2).[25,26] The signal at −140.9 ppm would be due to 1,2-dilithiodistannane (**7**), because of a ^1J(Sn−Sn) coupling constant of 1753 Hz and the formation of 1,2-dimethyldistannane

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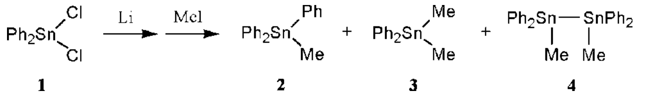
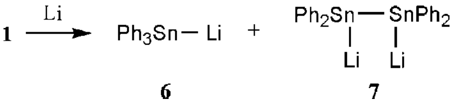


Scheme 1.



Scheme 2.

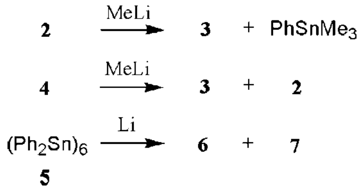
(**4**) by quenching with methyl iodide (Scheme 2). The signal for 1,1-dilithiostannane was not observed. The **6**-to-**7** ratio was estimated to be about 3 : 4 by signal intensities.

The ^{13}C NMR signals for **7** can be completely assigned from two sets of coupling satellites resulting from an Sn–Sn bond. The α-carbon in the phenyl ring of **7** resonated at 164.3 ppm. The α-carbon next to the anionic center is reported to appear at low field[25] with two sets of coupling satellites of ^1J(Sn–C) (220 and 229 Hz) and ^2J(Sn–C) (24 Hz). (The α-carbon of **6** resonated at 166.6 ppm with ^1J(Sn–C) of 255 and 266 Hz (166.6 ppm with ^1J(Sn–C) of 260 Hz in Refs 25 and 26). The assignment of the ^{13}C signals of **6** was reported in Ref. 25.) The β-carbon of **7** resonated at 140.4 ppm with ^2J(Sn–C) (38 Hz) and ^3J(Sn–C) (16 Hz). In ^{7}Li NMR, only one singlet appeared, at 0.58 ppm, suggesting the rapid exchange between lithium cations of **6** and **7**.

The intensity of the signal for **7** in ^{119}Sn NMR gradually decreased with the gradual formation of black precipitates. After 2 weeks, the signal for **7** completely disappeared and only one signal for **6** was observed.

Control experiments

No evidence for the formation of 1,1-dilithiostannane by NMR studies suggests that dimethyldiphenylstannane (**3**) arises from secondary reactions. Reaction of methyltriphenylstannane (**2**) with methyllithium gave **3** and trimethylphenylstannane in 35% and 14% yields respectively (Scheme 3). Reaction of 1,2-dimethyldistannane (**4**) with methyllithium gave **2** and **3** in 30% and 38% yields respectively (Scheme 3). In the reduction of **1**, the yield of **3** decreased remarkably to 4% in the absence of excess lithium (Scheme 1). Thus, compound **3** arises from the reaction of **2** and/or **4** with methyllithium generated by the reaction of methyl iodide with excess lithium.



Scheme 3.

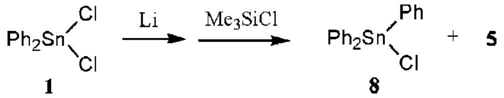
Reaction of $(Ph_2Sn)_6$ (**5**)[27] with excess lithium gave triphenylstannyllithium (**6**) as a major product together with 1,2-dilithiodistannane (**7**; Scheme 3). The **6**-to-**7** ratio was estimated to be 3 : 1 by signal intensities in ^{119}Sn NMR. Thus, triphenylstannyllithium (**6**) arises mainly from the reduction of an initially formed **5**. 1,2-Phenyl migration must occur in the formation of **6** from **5**. Such a migration of a phenyl group has been reported.[28]

Trapping 6 and 7 with other electrophiles

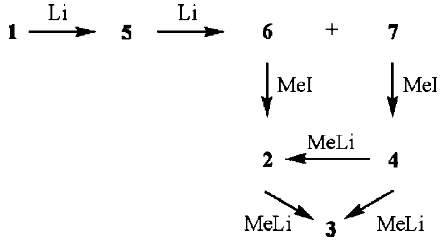
To avoid the formation of **3** by the reaction of **2** and/or **4** with methyllithium generated in the reaction mixture, the mixture was treated with dimethyl sulfate to give **5** (21%), **4** (13%) and **3** (2%). Thus, the formation of **3** was greatly suppressed using dimethyl sulfate instead of methyl iodide. Chlorotrimethylsilane was also used as a trapping reagent. However, the reaction became complicated, and only chlorotriphenylstannane (**8**; 9%) and $(Ph_2Sn)_6$ (**5**; 9%) were identifiable. Compounds **8** and **5** arise from the halophilic substitution of **6** and the oxidation of **7** respectively (Scheme 4).

CONCLUSIONS

Reduction of dichlorodiphenylstannane with lithium gave initially $(Ph_2Sn)_6$ (**5**), which was further reduced to afford triphenyllithium (**6**) and 1,2-dilithiodistannane (**7**). 1,1-Dilithiostannane, an expected intermediate in the reduction of dichlorodiphenylstannane, was not detected by NMR study because of different reaction conditions from those in a previous report in Ref. 20, reaction of **1** with lithium (four equivalents) in THF was reported to occur exothermally. However, treatment of the reduction mixture with methyl iodide gave 1,1-dimethylstannane (**3**) through the reaction of **2** and/or **4** with methyllithium (Scheme 5).



Scheme 4.



Scheme 5.

EXPERIMENTAL

General procedure

All reactions were carried out under argon. THF used in the synthesis was distilled from sodium benzophenone ketyl under argon atmosphere. C_6D_6 for NMR lock was distilled from sodium benzophenone ketyl under argon atmosphere. ^{1}H (400 MHz or 300 MHz) and ^{13}C NMR (100 MHz or 75 MHz) spectra were recorded on a Bruker AM-400, an ARX-400 or AC-300 spectrometer with tetramethylsilane as an internal standard. Although $^{n}J(\mathrm{Sn}-^{13}\mathrm{C})$ couplings were observed in ^{13}C NMR spectra as satellite signals, most of the $^{n}J(^{119}\mathrm{Sn}-^{13}\mathrm{C})$ and $^{n}J(^{117}\mathrm{Sn}-^{13}\mathrm{C})$ couplings could not be estimated because of broadening. ^{119}Sn NMR (149 MHz) spectra were recorded on a Bruker ARX-400 spectrometer with tetramethylstannane as an external standard. Wet column chromatography (WCC) was carried out with Merck Kieselgel 60 (SiO_2). Preparative thin-layer chromatography (PTLC) was carried out with Merck Kieselgel 60 PF_{254} (Art. No. 7747). Preparative gel-permeation chromatography (GPC) was carried out on an LC-918 (Japan Analytical Ind. Co., Ltd) with JAIGEL-1H and -2H columns. Elemental analyses were carried out at the Microanalytical Laboratory of Chemical Analytical Center, Saitama University.

Reduction of dichlorodiphenylstannane (1) with excess lithium: trapping of the intermediates by methyl iodide

A mixture of dichlorodiphenylstannane (112 mg, 0.32 mmol) and lithium (19 mg, 2.67 mmol) in THF (4 ml) was stirred at room temperature for 2 h. After treatment of the reaction mixture with methyl iodide (0.5 ml, 8.03 mmol), aqueous NH_4Cl was added and the resulting mixture was extracted with hexane. After the usual work-up, the residue was subjected to WCC (hexane : ethyl acetate, 50 : 1) to give dimethyldiphenylstannane (**3**; 20 mg, 21%) and the mixture (30 mg) containing methyltriphenylstannane (**2**) and 1,2-dimethyl-1,1,2,2-tetraphenyldistannane (**4**). Further separation of the mixture by PTLC (hexane : ethyl acetate, 50 : 1) afforded **2** (15 mg, 13%) and **4** (11 mg, 12%). **2**: m.p. 58–60 °C. ^{1}H NMR ($CDCl_3$): δ 0.71 (s, ^{2}J(Sn–H) = 54, 56 Hz, 3H, Sn–Me), 7.35–7.38 (m, 9H), 7.54–7.56 (m, 6H). ^{13}C NMR ($CDCl_3$): δ −10.5 (^{1}J(Sn–C) = 379 Hz, Sn–Me), 128.5 (J(Sn–C) = 50 Hz, C_2), 128.9 (J(Sn–C) = 11 Hz, C_4), 136.8 (J(Sn–C) = 37 Hz, C_3), 139.2 (^{1}J(Sn–C) = 489, 512 Hz, C_1). ^{119}Sn NMR ($CDCl_3$): δ −92.4. Anal. Found: C, 62.58; H, 4.83. Calc. for $C_{19}H_{18}Sn$: C, 62.51; H, 4.97%. **3**: ^{1}H NMR ($CDCl_3$): δ 0.50 (s, ^{2}J(Sn–H) = 54, 56 Hz, 6H, Sn–Me), 7.30–7.36 (m, 6H), 7.45–7.56 (m, 4H). ^{13}C NMR ($CDCl_3$): δ −10.1 (^{1}J(Sn–C) = 351, 368 Hz, Sn–Me), 128.3 (J(Sn–C) = 46 Hz, C_2), 128.6 (J(Sn–C) = 11 Hz, C_4), 136.3 (J(Sn–C) = 36 Hz, C_3), 140.7 (^{1}J(Sn–C) = 479, 504 Hz, C_1). ^{119}Sn NMR (THF–C_6D_6): δ −60.7. Anal. Found: C, 55.63; H, 5.21. Calc. for $C_{14}H_{16}Sn$: C, 55.50; H, 5.32%. **4**: m.p. 90–91 °C. ^{1}H NMR ($CDCl_3$): δ 0.71 (s, J(Sn–H) = 14, 48, 50 Hz, 6H, Sn–Me), 7.27–7.31 (m, 12H), 7.39–7.52 (m, 8H). ^{13}C NMR ($CDCl_3$): δ −9.0 (J(Sn–C) = 57, 260, 271 Hz, Sn–Me), 128.4 (J(Sn–C) = 11, 46 Hz, C_2 and C_4), 136.9 (J(Sn–C) = 8, 40 Hz, C_3), 140.2 (^{1}J(Sn–C) = 60, 374, 391 Hz, C_1). ^{119}Sn NMR ($CDCl_3$): δ −131.2 (^{1}J(Sn–Sn) = 4241 Hz). Anal. Found: C, 54.49; H, 4.48. Calc. for $C_{26}H_{26}Sn_2$: C, 54.22; H, 4.55%.

Trapping of the intermediates by methyl iodide after removal of excess lithium

A mixture of dichlorodiphenylstannane (163 mg, 0.47 mmol) and lithium (25 mg, 3.62 mmol) in THF (4 ml) was stirred at room temperature for 2 h. After removal of excess lithium by filtration, the resulting solution was treated with methyl iodide (0.2 ml, 3.26 mmol). After the usual work-up, the residue was subjected to WCC (hexane : ethyl acetate, 50 : 1) to give methyltriphenylstannane (**2**; 14 mg, 9%), dimethyldiphenylstannane (**3**; 6 mg, 4%) and a mixture (81 mg) containing 1,2-dimethyl-1,1,2,2-tetraphenyldistannane (**4**). Further separation of the mixture by GPC afforded **4** (51 mg, 38%).

NMR study of the reaction of dichlorodiphenylstannane (1) with excess lithium

A mixture of dichlorodiphenylstannane (**1**; 263 mg, 0.76 mmol) and lithium (47 mg, 6.73 mmol) in THF (2.4 ml) was stirred at room temperature for 2 h. An aliquot (0.7 ml) of the resulting deep-red solution was placed in an NMR tube with C_6D_6 (0.3 ml), degassed by freeze–pump–thaw cycles and sealed. **6**: ^{13}C NMR (THF–C_6D_6): δ 123.5 (C_4), 126.2 (C_3), 138.9 (^{2}J(Sn–C) = 54 Hz, C_2), 166.6 (^{1}J(Sn–C) = 255, 266 Hz, C_1). ^{119}Sn NMR (THF–C_6D_6): δ −105.3. The assignment of the ^{13}C signals of **6** was reported in Ref. 25. **7**: ^{13}C NMR (THF–C_6D_6): δ 122.2 (C_4), 125.6 (C_3), 140.4 (^{2}J(Sn–C) = 38 Hz, ^{3}J(Sn–C) = 16 Hz, C_2), 164.3 (^{1}J(Sn–C) = 220, 229 Hz, ^{2}J(Sn–C) = 24 Hz, C_1). ^{119}Sn NMR (THF–C_6D_6): δ −140.9 (^{1}J(Sn–Sn) = 1753 Hz). The assignment of the carbon atoms of **7** was carried out by comparing with the assignment of those of **6** in Ref. 25.

Reaction of methyltriphenylstannane (2) with methyllithium

To a THF (2 ml) solution of methyltriphenylstannane (**2**; 79 mg, 0.22 mmol) was added methyllithium (1.02 M in diethyl ether; 0.37 ml, 0.38 mmol) at room temperature. Volatile components and materials insoluble in dichloromethane were removed. The residue (37 mg) contains 35% of **3**, 14% of trimethylphenylstannane and 8% of recovered **2** by ^{1}H NMR estimation.

Reaction of 1,2-dimethyl-1,1,2,2-tetraphenyldistannane (4) with methyllithium

To a THF (2 ml) solution of 1,2-dimethyl-1,1,2,2-tetraphenyldistannane (**4**; 22 mg, 0.038 mmol) was added methyllithium (1.02 M in diethyl ether; 0.12 ml, 0.12 mmol) at room temperature. Similar work-up as above gave 17 mg of a crude mixture that contains 38% of **3** and 30% of **2** by ^{1}H NMR estimation.

Reduction of $(Ph_2Sn)_6$ (5) with lithium monitored by ^{119}Sn NMR

A mixture of **5**[27] (226 mg, 0.14 mmol) and lithium (18 mg, 2.65 mmol) in THF (2.6 ml) was stirred at room temperature for 0.5 h. An aliquot (0.7 ml) of the resulting deep-red solution was placed in an NMR tube with C_6D_6 (0.3 ml), degassed by freeze–pump–thaw cycles and sealed. ^{119}Sn NMR: δ −108.9, −142.3 (^1J(Sn–Sn) = 1732 Hz).

Trapping of the intermediates by dimethyl sulfate

A mixture of dichlorodiphenylstannane (305 mg, 0.89 mmol) and lithium (48 mg, 6.92 mmol) in THF (6 ml) was stirred at room temperature for 2 h. The reaction mixture was treated with a THF (5 ml) solution of dimethyl sulfate (0.9 ml, 9.95 mmol). After the usual work-up, the residue was subjected to WCC (hexane : ethyl acetate, 50 : 1) followed by GPC to give methyltriphenylstannane (**2**; 41 mg, 13%), dimethyldiphenylstannane (**3**; 5 mg, 2%) and 1,2-dimethyl-1,1,2,2-tetraphenyldistannane (**4**; 54 mg, 21%).

Trapping of the intermediates by chloro-trimethlsilane

A mixture of dichlorodiphenylstannane (298 mg, 0.87 mmol) and lithium (46 mg, 6.67 mmol) in THF (6 ml) was stirred at room temperature for 2 h. The reaction mixture was treated with a THF (4 ml) solution of chlorotrimethylsilane (0.3 ml, 2.36 mmol). After the usual work-up, the residue was subjected to WCC (hexane : ethyl acetate, 50 : 1) to afford a mixture (60 mg) containing **5** and chlorotriphenylstannane (**8**). The yields of **5** and **8** were estimated to be 9% and 9% respectively by ^{1}H NMR.

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