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Reinvestigation on the Halogenation of 1,1,2,3,4,5-Hexaphenylstannole

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ABSTRACT: *Halogenation of 1,1,2,3,4,5-hexaphenylstannole was reinvestigated. Reaction of the stannole with 2 equiv. of bromine gave 1-bromo-4-dibromophenylstannyl-1,2,3,4-tetraphenyl-1,3-butadiene. Reaction of the stannole with iodine gave similar results. Reaction of the stannole with 1 equiv. of bromine or iodine afforded 1-halo-4-halodiphenylstannyl-1,2,3,4-tetraphenyl-1,3-butadiene, resulting from halogenation with the cleavage of the bond between tin and vinyl carbon.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:349–353, 2001

INTRODUCTION

1,1-Dihalometalloles of group 14 elements are well known as good precursors for the dianions of the corresponding metalloles, fascinating reactive species with considerable aromaticity [1–3]. In contrast to the well-investigated dianions of siloles and germoles, there are few reports on the dianion of a stannole, although several 1,1-dihalostannoles have been synthesized and their reactivities with various nucleophiles have been studied [4,5]. In the course of our studies on tin-containing compounds having unique structure [6], we attempted to study 1,1-dihalostannoles as precursors for the dianion of the stannole. Zuckerman et al. reported that the reaction of 1,1-diphenylstannoles with halogens gave 1,1-dihalostannoles. They assigned the 1,1-dihalostannole structure on the basis of IR and Mössbauer spectra and elemental analysis [4]. Our interest in preparing the 1,1-dihalostannoles led us to reinvestigate the reaction of 1,1,2,3,4,5-hexaphenylstannole with halogens. Reinvestigation revealed the formation of the ring-opened halogenated products instead of the 1,1-dihalostannoles. We report herein the revised structures of the resulting products of the halogenation of 1,1,2,3,4,5-hexaphenylstannole.

RESULTS AND DISCUSSION

Bromination of Hexaphenylstannole (1)

1,1,2,3,4,5-Hexaphenylstannole (**1**) was synthesized by the reported procedure [4,7]. The structure of stannole **1** that was based on elemental analysis and on Mössbauer, and IR spectra [4] was unambiguously established by ^{1}H, ^{13}C NMR spectra, and X-ray analysis [7]. Bromination of **1** was carried out according to procedures in the literature [4]. Two equiv. of bromine in carbon tetrachloride was added to a solution of **1** in carbon tetrachloride at $-20°C$. The original yellow color lightened with the addition of bromine. After complete addition of bromine, the color of the solution turned reddish orange. After removal of the solvent, the residue was recrystallized from methylene chloride–ethanol to afford colorless crystals. The ^{13}C NMR spectrum suggested that the product was not a 1,1-dibromostannole but had an unsymmetrical structure (Scheme 1). The structure

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Dedicated to Professor Naoki Inamoto, Prof. Emeritus of The University of Tokyo, on the occasion of his 72nd birthday.

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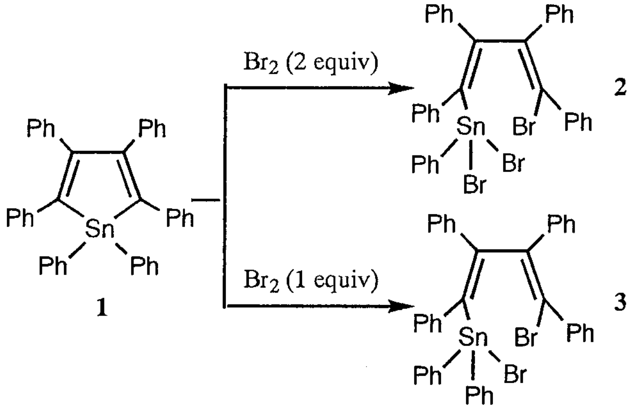
was established by X-ray crystallographic analysis to be **2** (Figure 1). An ORTEP drawing shows that two bromine atoms were introduced onto the tin, and one phenyl group still remained on the tin. The compound **2** may be produced either by the initial cleavage of the Sn–C(vinyl) bond with the addition of bromine followed by substitution of a phenyl group on Sn by a bromine atom or by the initial substitution of a phenyl group on Sn by a bromine atom, followed by ring opening with the addition of bromine.

To examine the stage of the ring opening, the reaction of **1** with one equiv. of bromine was carried out. Bromine (1 equiv.) in carbon tetrachloride was added to a solution of **1** in carbon tetrachloride at −20°C. After removal of the solvent, the residue was recrystallized from methylene chloride–ethanol to afford **3**, the structure of which was determined by ^{13}C NMR spectroscopy (Scheme 1) and finally established by X-ray crystallographic analysis. The bromination of **1** is found to occur first at the endocyclic Sn–vinyl bond to give **3**, in sharp contrast to the known ease of cleavage of the Sn–C bond in the order of Sn–aromatic > –vinyl > –alkyl [8–10]. The bromination of **1** at the endo-cyclic Sn–vinyl bond also occurred even at low temperature in other solvents (Table 1). The cleavage of the metal (Si, Ge, Sn)–vinyl carbon bond also occurred in the halogenation of 1,1-dimethylmetalloles [11].



SCHEME 1

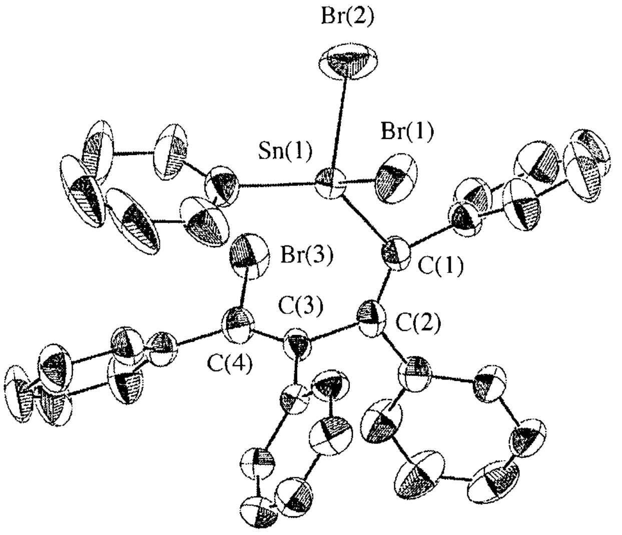


FIGURE 1 ORTEP drawing of **2** with thermal ellipsoids plots (40% probability for nonhydrogen atoms). Selected bond lengths (Å) and angles (°): Sn(1)–C(1), 2.136(5); C(1)–C(2), 1.336(6); C(2)–C(3), 1.491(5); C(3)–C(4), 1.339(6); Sn(1)–C(1)–C(2), 120.0(3); C(2)–C(3)–C(4), 121.9(8).

Iodination of Hexaphenylstannole (1)

Iodination of 1,1,2,3,4,5-hexaphenylstannole (**1**) was reported to give 1,1-diiodo-2,3,4,5-tetraphenylstannole [4]. However, the reinvestigation by us showed

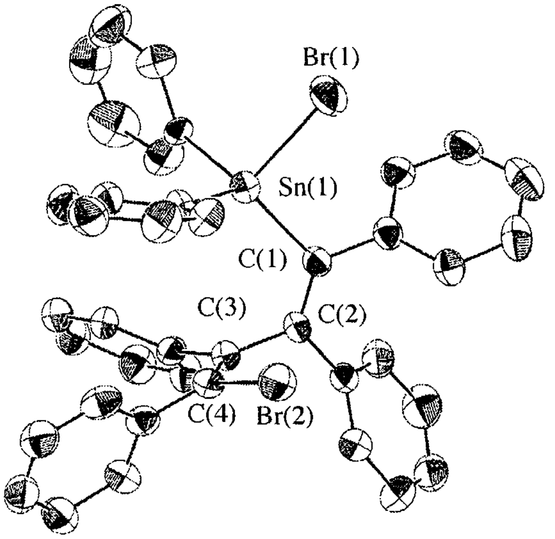


FIGURE 2 ORTEP drawing of **3** with thermal ellipsoids plots (40% probability for nonhydrogen atoms). Selected bond lengths (Å) and angles (°): Sn(1)–C(1), 2.149(6); C(1)–C(2), 1.334(7); C(2)–C(3), 1.488(7); C(3)–C(4), 1.332(8); Sn(1)–C(1)–C(2), 121.1(4); C(2)–C(3)–C(4), 124.2(5).

TABLE 1 Bromination of **1**

$$1 + Br_2(2\ \text{equiv}) \xrightarrow[\text{temperature}]{\text{solvent}} 2$$

Solvents	*Temp (°C)*	*Yield of **2** (%)*
CCl_4	−20	63
CH_2Cl_2	−40	54
THF	−40	45
Et_2O	−40	46

that the reaction of **1** with iodine (2 equiv.) in carbon tetrachloride at 0°C gave **4** having a structure similar to that of 3. The iodination of **1** also occurred exclusively at the endocyclic Sn–vinyl bond. In contrast to the bromination of **1**, the triiodo-substituted product **5** was not obtained, probably due to steric reasons. However, the reaction of **1** with an excess amount of iodine gave the triiodo-substituted **5** together with **4** (ratio; about 1:1). After repetitive recrystallization, **5** was obtained in 16% yield. Exhaustive iodination of **1** also gave triiodo-substituted **5** (Scheme 2).

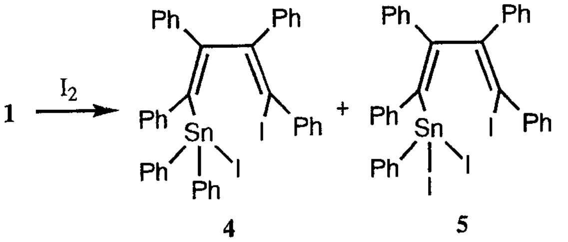
CONCLUSION

Halogenation of 1,1,2,3,4,5-hexaphenylstannole was reinvestigated under the same conditions previously reported [4]. The halogenation occurred at the Sn–vinyl bond in preference to that at the Sn–phenyl bond. The previously reported structures of products produced by halogenation of the stannole were not correct. The investigation on the synthesis of 1,1-dihalo-2,3,4,5-tetraphenylstannole is currently in progress.

EXPERIMENTAL

General Procedure

All reactions were carried out under argon. Tetrahydrofuran (THF) and diethyl ether used in the syntheses were distilled from sodium benzophenone ketyl under an argon atmosphere before use. Carbon tetrachloride was distilled from calcium hydride before use. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AM-400 or an ARX-400 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. ^{119}Sn NMR (149 MHz) spectra were recorded on a Bruker ARX-400 spectrometer in $CDCl_3$ with tetramethylstannane as an external standard. Wet column chromatography (WCC) was carried out with Merck Kieselgel 60 (SiO_2). All melting points were determined on a Mitamura Riken Kogyo MEL-TEMP apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Chemical Analytical Center, Saitama University. Data for the X-ray crystallographic analyses were collected on a Mac Science Xdip diffractometer with Mo Kα radiation (λ = 0.71073 Å), and the structures were solved by direct methods.



4 **5**

SCHEME 2

Preparation of 1,1,2,3,4,5-Hexaphenylstannole (1)

1,1,2,3,4,5-Hexaphenylstannole (**1**) was prepared according to the described method [4,7]. Compound **1** was purified by WCC (hexane:ethyl acetate = 20:1). **1**: ^{1}H NMR: δ 6.80–7.08 (m, 20H), 7.22–7.45 (m, 6H), 7.47–7.73 (m, 4H); ^{13}C NMR: δ 125.38 (d), 125.91 (d), 127.38 (d), 127.89 (d), 128.97 (d), 129.22 (d), 129.44 (d), 130.31 (d), 137.17 (d), 138.09 (s), 140.60 (s), 142.34 (s), 142.79 (s), 155.17 (s); ^{119}Sn NMR: δ −88.7.

Reaction of **1** *with Bromine (2 equiv.)*

Bromine (0.08 mL, 1.55 mmol) in carbon tetrachloride (5 mL) was added to a carbon tetrachloride (6 mL) solution of 1,1,2,3,4,5-hexaphenylstannole (**1**) (500 mg, 0.79 mmol) at −20°C. After gradual warming to room temperature, the solvent was removed. The residue was recrystallized from methylene chloride–ethanol to afford 1-bromo-4-dibromophenylstannyl-1,2,3,4-tetraphenyl-1,3-butadiene (**2**) (396 mg, 65%). Reaction of **1** with bromine (2 equiv.) in other solvents at −40°C was also carried out by a similar procedure. **2**: m.p. 156–157°C (decomp) (recrystallized from methylene chloride-ethanol; 10:1). ^{1}H NMR: δ 6.61–6.63 (m, 2H), 6.90–6.97 (m, 4H), 7.01–7.06 (m, 6H), 7.13–7.33 (m, 9H), 7.43–7.46 (m, 2H), 7.73–7.76 (m, 2H); ^{13}C NMR: δ 126.88 (s), 127.43 (d), 127.52 (d), 127.81 (d), 127.87 (d), 127.88 (d), 128.14 (d), 128.21 (d), 128.32 (d), 129.20 (d), 129.70 (d), 129.75 (d), 129.78 (d), 129.93 (d), 130.92 (d), 135.06 (d), 136.84 (s), 137.08 (s), 138.14 (s), 139.04 (s), 141.11 (s), 143.24 (s), 146.54 (s), 155.19 (s); ^{119}Sn NMR: δ −102.4. Anal. calcd for $C_{34}H_{25}Br_3Sn$: C, 51.56; H, 3.18. Found: C, 51.44; H, 3.17.

Crystal and Experimental Data for **2** *at 298 K*

$C_{34}H_{25}Br_3Sn$, M = 791.99, triclinic, a = 10.6430(7), b = 11.7280(8), c = 13.7050(10) Å, α = 115.479(3), β = 89.927(2), γ = 96.188(4)°, V = 1533.4(2) Å^3, D_{calc} = 1.715 Mg m^{-3}, Z = 2, space group $P\bar{1}$. The non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were placed at calculated positions (d(C–H) = 0.96 Å). The final cycle of full-matrix least-squares refinement was based on 3852 observed reflections [$I > 3.00\sigma(I)$] and 343 variable parameters with R($_wR2$) = 0.068 (0.131).

Reaction of 1 *with Bromine (1 equiv.)*

Bromine (0.035 mL, 0.68 mmol) in carbon tetrachloride (4 mL) was added to a carbon tetrachloride (3 mL) solution of 1,1,2,3,4,5-hexaphenylstannole (**1**) (428 mg, 0.68 mmol) at -20°C. After gradual warming to room temperature, the solvent was removed. The residue was recrystallized from methylene chloride-ethanol to afford 1-bromo-4-bromodiphenylstannyl-1,2,3,4-tetraphenyl-1,3-butadiene (**3**) (432 mg, 80%). **3**: m.p. 165–166°C (decomp) (recrystallized from methylene chloride–ethanol; 10:1). ^{1}H NMR: δ 6.57–6.70 (m, 1H), 6.80–7.40 (m, 20H), 7.42–7.55 (m, 2H), 7.60–7.90 (m, 2H); ^{13}C NMR: δ 125.69 (s), 126.44 (d), 127.29 (d), 127.39 (d), 127.49 (d), 127.65 (d), 127.86 (d), 127.99 (d), 128.06 (d), 128.53 (d), 128.79 (d), 129.41 (d), 129.67 (d), 129.68 (d), 129.83 (d), 129.99 (d), 130.01 (d), 136.28 (d), 136.38 (d), 137.66 (s), 138.32 (s), 138.69 (s), 139.44 (s), 139.68 (s), 141.99 (s), 143.49 (s), 145.91 (s), 155.78 (s); ^{119}Sn NMR: δ -95.5. Anal. Calcd for $C_{40}H_{30}Br_2Sn$: C, 60.88; H, 3.83. Found: C, 60.79; H, 3.83.

Crystal and Experimental Data for 3 *at 298 K*

$C_{40}H_{30}Br_2Sn$, $M = 789.2$, monoclinic, $a = 10.0490(7)$, $b = 9.8310(7)$, $c = 33.834(2)$ Å, $\beta = 95.920(4)°$; $V = 3324.7(4)$ Å^3, $D = 1.577$ Mg m^{-3}, $Z = 4$, space group $P2_1/c$. The nonhydrogen atoms were refined anisotropically, and all the hydrogen atoms were placed at calculated positions (d(C–H) = 0.96 Å). The final cycle of full-matrix least-squares refinement was based on 5847 observed reflections [$I > 0.00\sigma(I)$] and 388 variable parameters with $R(_wR2) = 0.101$ (0.180).

Reaction of 1 *with Iodine (2 equiv.)*

Iodine (531 mg, 2.09 mmol) in carbon tetrachloride (20 mL) was added to a carbon tetrachloride (5 mL) solution of 1,1,2,3,4,5-hexaphenylstannole (**1**) (590 mg, 0.94 mmol) at 0°C. After gradual warming to room temperature, the solvent was removed. The residue was recrystallized from methylene chloride-ethanol to afford 1-iodo-4-iododiphenylstannyl-1,2,3,4-tetraphenyl-1,3-butadiene (**4**) (690 mg, 83%). **4**: m.p. 169°C (decomp) (recrystallized from methylene chloride-ethanol; 10:1). ^{1}H NMR: δ 6.42 (d, $J = 8$ Hz, 2H), 6.86–6.90 (m, 2H), 6.94–7.13 (m, 12H), 7.24–7.27 (m, 8H), 7.38 (d, $J = 7$ Hz, 2H), 7.48–7.49 (m, 2H), 7.63 (d, $J = 8$ Hz, 2H); ^{13}C NMR: δ 107.49 (s), 126.50 (d), 127.41 (d), 127.42 (d), 127.47 (d), 127.65 (d), 127.68 (d), 127.70 (d), 128.05 (d), 128.42 (d), 128.73 (d), 129.42 (d), 129.52 (d), 129.53 (d), 129.80 (d), 130.08 (d), 130.25 (d), 136.71 (d), 136.76 (d), 137.11 (s), 137.98 (s), 139.10 (s), 139.27 (s), 142.26 (s), 142.50 (s), 145.21 (s), 148.59 (s), 158.59 (s); ^{119}Sn NMR: δ -130.5. Anal. calcd for $C_{40}H_{30}I_2Sn$: C, 54.40; H, 3.42. Found: C, 54.30; H, 3.37.

Reaction of 1 *with Iodine (excess)*

Iodine (402 mg, 1.58 mmol) in carbon tetrachloride (10 mL) was added to a carbon tetrachloride (4 mL) solution of 1,1,2,3,4,5-hexaphenylstannole (**1**) (309 mg, 0.49 mmol) at 0°C. After gradual warming to room temperature over 6 hours, the solvent was removed. The residue was recrystallized from methylene chloride-ethanol to afford 1-iodo-4-diiodophenylstannyl-1,2,3,4-tetraphenyl-1,3-butadiene (**5**) (72 mg, 16%). **5**: m.p. 152–154°C (decomp) (recrystallized from methylene chloride-ethanol; 10:1). ^{1}H NMR: δ 6.47 (d, $J = 7$ Hz, 2H), 6.87–7.06 (m, 10H), 7.20–7.35 (m, 9H), 7.53 (d, $J = 7$ Hz, 2H), 7.86–7.89 (m, 2H); ^{13}C NMR: δ 108.36 (s), 127.42 (d), 127.58 (d), 127.74 (d), 127.76 (d), 127.88 (d), 127.91 (d), 127.97 (d), 128.13 (d), 129.01 (d), 129.78 (d), 129.93 (d), 129.97 (d), 130.07 (d), 130.61 (d), 135.49 (d), 136.45 (s), 136.81 (s), 139.66 (s), 140.53 (s), 142.04 (s), 144.49 (s), 148.15 (s), 156.79 (s); ^{119}Sn NMR: δ -221.9. Anal. calcd for $C_{34}H_{25}I_3Sn$: C, 43.77; H, 2.70. Found: C, 44.20; H, 2.70.

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