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Synthesis and photochemical reactions of 1,2,7-chalcogenadistannacycloheptanes†

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1,2,7-Chalcogenadistannacycloheptanes were synthesized by the reactions of 1,4-bis(bromostannyl) butane with appropriate chalcogenation reagents. Irradiation of the 1,2,7-thiadistannacycloheptane with a low-pressure mercury lamp (254 nm) gave 1,3,5,2,4,6-trithiatristannin. Irradiation of 1,3,5,2,4,6-trithiatristannin with a low-pressure mercury lamp in the presence of either cyclotrisiloxane or 2,3-dimethyl-1,3-butadiene gave a complex mixture. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: 1,4-bis(bromostannyl)butane; 1,2,7-chalcogenadistannacycloheptane; photochemical reaction; 1,3,5,2,4,6-trithiatristannin

INTRODUCTION

Double-bond compounds between heavier Group 14 and Group 16 elements are known to be useful building blocks for the synthesis of chalcogen-containing heterocyclic compounds via cycloaddition reactions such as [2 + 2]cycloaddition and 1,3-dipolar cycloaddition, e.g. see the reviews of Raabe and Michl[1] and Barrau *et al.*[2] Such double-bond species are known to be generated transiently by the thermolysis or the photolysis of 1,3,5-trichalcogenane or 1,2,7-chalcogenadimetallacycloheptane derivatives, as confirmed by trapping reactions with various reagents,[3–8] a useful method for the synthesis of heterocyclic compounds having Group 14 elements. To the best of our knowledge, however, there is no report on the formation of tin–chalcogen double-bond compounds by the thermolysis or the photolysis of tin-containing heterocyclic compounds. We have already reported the thermal reaction of the 1,3,5,2,4,6-trichalcogenatristannin with nitrile oxide to give the 1,3,5,2-oxachalcogenazastannole and its unusual dissociation behavior to generate a tin–chalcogen double-bond compound[9] (Scheme 1). We report herein the photochemical generation of tin–chalcogen double-bond compounds from 1,2,7-chalcogenadistannacycloheptanes. Photochemical reactions of 1,3,5,2,4,6-trichalcogenatristannins were also described.

RESULTS AND DISCUSSION

Photochemical reactions of 1,3,5,2,4,6-trichalcogenatristannins

1,3,5,2,4,6-Trichalcogenatristannins were expected to generate tin–chalcogen double-bond compounds by irradiation.[9] The absorption bands were observed at 238 nm (ε 6880) for 1,3,5,2,4,6-trithiatristannin (**1**) in hexane and 266 nm (ε 6340) and 246 nm (ε 6360) for 1,3,5,2,4,6-triselenatristannin (**2**) in tetrahydrofuran (THF). A complex mixture was obtained by irradiation of **1** with a low-pressure mercury lamp (254 nm) in the presence of a trapping reagent for the tin–chalcogen double-bond compound. The intermediacy of dimethylsilaneselone was evidenced by the photolysis of 1,3,5,2,4,6-cyclotrisilaselenanes in the presence of cyclotrisiloxane to give the insertion products; see Refs 4 and 5. The compounds having a double bond between Group 14 and 16 elements reacted with 2,3-dimethyl-1,3-butadiene to give [4 + 2]cycloadducts for X = Si, Ge[10] and for X = Sn;[11] stannylene reacted with 2,3-dimethyl-1,3-butadiene to give [4 + 1]cycloadducts, e.g. see the review of Neumann.[12] Irradiation of 1,3,5,2,4,6-triselenatristannin (**2**) with a low-pressure mercury lamp also gave a complex mixture (Scheme 2).

Synthesis of 1,2,7-chalcogenadistannacycloheptanes

The 1,2,7-chalcogenadistannacycloheptanes are expected to be suitable precursors of tin–chalcogen double-bond

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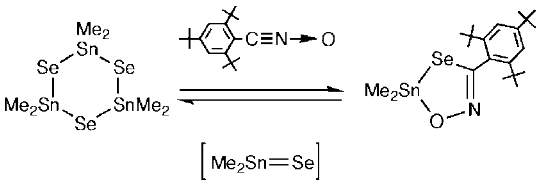
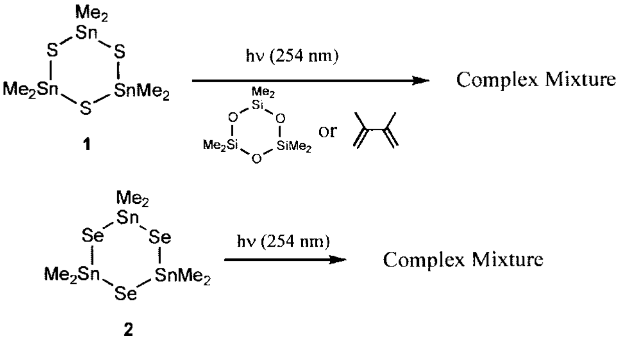


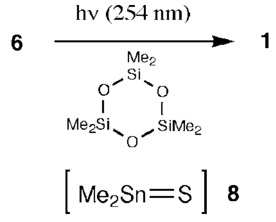
Scheme 1.



Scheme 2.

compounds. The formation of the dimethylsilanethione, $Me_2Si{=}S$, was proposed in the photochemical reaction of 1,2,7-thiadisilacycloheptane.[8] Reaction of iodo(*p*-methoxyphenyl)stannane (**3**) with the 1,4-di-Grignard reagent [$BrMg(CH_2)_4MgBr$] gave 1,4-distannylbutane (**4**). Bromination of **4** afforded 1,4-bis(dibromostannyl)butane (**5**). The *p*-methoxyphenyl group on the tin atom is known to be easily substituted by halogen.[13]

Treatment of **5** with sodium sulfide or Li_2Se gave 1,2,7-thiadistannacycloheptane (**6**) and 1,2,7-selenadistannacycloheptane (**7**) in 85% and 24% yields respectively (Scheme 3). Compound **7** was so labile that it decomposed to red selenium over a few days.



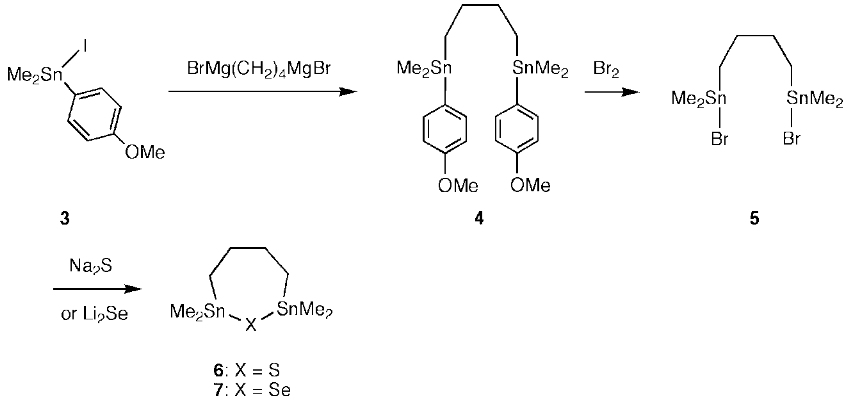
Scheme 4.

Photochemical reaction of 1,2,7-thiadistannacycloheptane (6)

Since the absorption band of **6** was found at 240 nm (ε 3090) in THF, photochemical reactions of **6** was investigated using a low-pressure mercury lamp (254 nm). Irradiation of a THF solution of 1,2,7-thiadistannacycloheptane (**6**) at room temperature in the presence of cyclotrisiloxane[4,5] gave 1,3,5,2,4,6-trithiatristannin (**1**) as a main product. No product derived by the reaction of dimethylstannanethione with cyclotrisiloxane was obtained. Irradiation of a THF solution of **6** in the presence of 2,3-dimethyl-1,3-butadiene[10,11] (see above) gave **1** with unidentifiable polymeric material. No cycloadduct between 2,3-dimethyl-1,3-butadiene and dimethylstannylene was obtained.[12] The formation of 1,3,5,2,4,6-trithiatristannin (**1**) can be explained in terms of trimerization of the initially formed dimethylstannanethione, $Me_2Sn{=}S$ (**8**; Scheme 4).

CONCLUSIONS

1,2,7-Chalcogenadistannacycloheptanes were synthesized by the reaction of 1,4-bis(bromostannyl)butane with appropriate chalcogenation reagents. Irradiation of the 1,2,7-thiadistannacycloheptane with a low-pressure mercury lamp gave the 1,3,5,2,4,6-trithiatristannin, suggesting the formation of stannanethione.



Scheme 3.

EXPERIMENTAL

General procedure

All reactions were carried out under argon. THF and hexane used in the synthesis were distilled from sodium benzophenone ketyl under argon atmosphere. Magnesium (turnings) was purchased from Wako Pure Chemical Industries, Ltd. ^{1}H (400 MHz), ^{13}C NMR (101 MHz) and ^{119}Sn NMR (149 MHz) spectra were recorded on a Bruker AM-400 or a DRX-400 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. UV–vis spectra were measured on a JASCO Ubest V-560 spectrometer. Preparative gel-permeation chromatography (GPC) was carried out on a LC-918 (Japan Analytical Ind. Co., Ltd) with JAIGEL-1H and -2H columns. All irradiations were carried out with a 10 W low-pressure mercury lamp (254 nm) using a quartz cell. 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 Material and Life Science Research Center of Saitama University.

Irradiation of 1,3,5,2,4,6-trithiatristannin (1) in the presence of trapping reagent

A deoxygenated hexane (10 ml) solution of 1,3,5,2,4,6-trithiatristannin (**1**)[14] (37 mg, 0.07 mmol) in the presence of hexamethylcyclotrisiloxane (825 mg, 3.72 mmol) or 2,3-dimethyl-1,3-butadiene (0.2 ml, 1.77 mmol) was irradiated at −78 °C for 48 h. Removal of volatile components gave a complex mixture.

Irradiation of 1,3,5,2,4,6-triselenatristannin (2)

A deoxygenated THF (10 ml) solution of 1,3,5,2,4,6-triselenatristannin (**2**)[14] (93 mg, 0.14 mmol) was irradiated at room temperature for 14 h. Removal of volatile components gave a complex mixture.

Preparation of 1,4-bis[(*p*-methoxyphenyl)-dimethylstannyl]butane (4)

To a THF (8 ml) solution of 1,4-butanedimagnesium dibromide prepared from 1,4-dibromobutane (0.45 ml, 3.81 mmol) and magnesium (185 mg, 7.62 mmol) was added a THF (8 ml) solution of iodo(*p*-methoxyphenyl)dimethylstananne (**3**)[15] (2.577 g, 6.73 mmol) at room temperature and the resulting mixture was heated under reflux overnight. After addition of aqueous NH_4Cl to the reaction mixture, the organic layer was extracted with methylene chloride. The organic layer was dried over anhydrous magnesium sulfate. Removal of volatile components gave the crude 1,4-bis[(*p*-methoxyphenyl)dimethylstannyl]butane (**4**) (1.866 g, 98%). An aliquot (211 mg) of the crude product was subjected to GPC to afford pure **4** (120 mg, 56%) as a colorless oil.

4. ^{1}H NMR: δ 0.31 (s, 12H, ^{2}J(Sn–H) = 52 Hz, Sn–Me), 1.01–1.18 (m, 4H, α-CH_2), 1.58–1.72 (m, 4H, β-CH_2), 3.86 (s, 6H, OMe), 6.98 (d, J = 9 Hz, 4H, *m*-CH), 7.39–7.51 (m, 4H, *o*-CH). ^{13}C NMR: δ −10.62 (J(Sn–C) = 317, 331 Hz, Sn–Me), 10.75 (J(Sn–C) = 359, 376 Hz, α-C), 31.04 (J(Sn–C) = 21, 58 Hz, β-C), 54.90 (OMe), 113.95 (J(Sn–C) = 48 Hz, *o*-C), 132.07 (J(Sn–C) = 434, 454 Hz, *ipso*-C), 137.00 (J(Sn–C) = 39 Hz, *m*-C), 159.80 (J(Sn–C) = 10 Hz, *p*-C). ^{119}Sn NMR: δ −29.4. Anal. Found: C, 46.72; H, 6.08. Calc. for $C_{22}H_{34}O_2Sn_2$: C, 46.53; H, 6.03%.

Preparation of 1,4-bis[(bromodimethyl)stannyl]-butane (5)

To a carbon tetrachloride (20 ml) solution of 1,4-bis[(*p*-methoxyphenyl)dimethylstannyl]butane (**4**) (1.477 g, 2.60 mmol) was added a carbon tetrachloride (10 ml) solution of bromine (0.27 ml, 5.24 mmol) at room temperature. The mixture was allowed to stand for 1 h at room temperature and the volatile components were removed. The residue was purified by GPC to give 1,4-bis[(bromodimethyl)stannyl]butane (**5**; 818 mg, 61%).

5. M.p. 61–63 °C (recrystallization from methylene chloride + hexane). ^{1}H NMR: δ 0.76 (s, 12H, ^{2}J(Sn–H) = 56 Hz, Sn–Me), 1.36–1.51 (m, 4H, α-CH_2), 1.74–1.78 (m, 4H, β-CH_2). ^{13}C NMR: δ −1.81 (J(Sn–C) = 320, 335 Hz, Sn–Me), 17.70 (J(Sn–C) = 368, 385 Hz, α-C), 29.48 (J(Sn–C) = 25, 72 Hz, β-C). ^{119}Sn NMR: δ 139.5. Anal. Found: C, 18.63; H, 3.65. Calc. for $C_8H_{20}Br_2Sn_2$: C, 18.71; H, 3.92%.

Preparation of 2,2,7,7-tetramethyl-1,2,7-thiadistannacycloheptane (6)

To a methanol (25 ml) solution of 1,4-bis[(bromodimethyl)stannyl]butane (**5**; 292 mg, 0.57 mmol) was added sodium sulfide (163 mg, 0.68 mmol) at room temperature. The resulting mixture was allowed to stand for 5 h. The reaction was quenched by the addition of aqueous NH_4Cl and extracted with methylene chloride. The organic layer was dried over anhydrous magnesium sulfate. Removal of volatile components gave 2,2,7,7-tetramethyl-1,2,7-thiadistannacycloheptane (**6**; 184 mg, 85%) as a pale yellow oil.

6. ^{1}H NMR: δ 0.44 (s, 12H, ^{2}J(Sn–H) = 52, 54 Hz, Sn–Me), 1.12–1.18 (m, 4H, α-CH_2), 1.86–2.14 (m, 4H, β-CH_2). ^{13}C NMR: δ −2.94 (J(Sn–C) = 321, 336 Hz, Sn–Me), 14.41 (J(Sn–C) = 351, 368 Hz, α-C), 26.74 (J(Sn–C) = 31 Hz, β-C). ^{119}Sn NMR: δ 95.4. Anal. Found: C, 25.08; H, 4.98. Calc. for $C_8H_{20}SSn_2$: C, 24.91; H, 5.24%.

Preparation of 2,2,7,7-tetramethyl-1,2,7-selenadistannacycloheptane (7)

To a THF (5 ml) solution of 1,4-bis[(bromodimethyl)stannyl]butane (**5**; 126 mg, 0.24 mmol) was added a THF (5 ml) solution of Li_2Se prepared from elemental selenium (19 mg, 0.24 mmol) and Super Hydride® (1.0 M in THF; 0.55 ml, 0.55 mmol) at room temperature. The resulting mixture was allowed to stand for 1 h. The volatile components were removed and materials insoluble in methylene chloride were separated by filtration. The methylene chloride was removed and the residue was purified by GPC to afford 2,2,7,7-tetramethyl-1,2,7-selenadistannacycloheptane (**7**) (25 mg, 24%) as a yellow oil.

7. ^{1}H NMR: δ 0.51 (s, 12H, $^2J(\mathrm{Sn{-}H}) = 52$ Hz, Sn–Me), 1.11–1.28 (m, 4H, α-CH_2), 1.86–2.15 (m, 4H, β-CH_2). ^{13}C NMR: δ −3.19 ($J(\mathrm{Sn{-}C}) = 305$, 319 Hz, Sn–Me), 14.10 ($J(\mathrm{Sn{-}C}) = 342$, 359 Hz, α-C), 27.04 ($J(\mathrm{Sn{-}C}) = 14$, 31 Hz, β-C). ^{119}Sn NMR: δ 57.5. Anal. Found: C, 22.98; H, 4.56. Calc. for $C_8H_{20}SeSn_2$: C, 22.21; H, 4.66%.

Photochemical reaction of 1,2,7-thiadistannacycloheptane (6) in the presence of hexamethylcyclotrisiloxane

A deoxygenated THF (10 ml) solution of 1,2,7-thiadistannacycloheptane (**6**; 84 mg, 0.22 mmol) in the presence of hexamethylcyclotrisiloxane (227 mg, 1.02 mmol) was irradiated at room temperature for 4 h. The insoluble material was removed by filtration and the solvent was evaporated to give the mixture (100 mg) containing 1,3,5,2,4,6-trithiatristannin (**1**) and the recovered **6**. The residue was subjected to GPC to afford pure **1** (10 mg, conversion 31%) and **6** (13 mg, conversion 16%).

Photochemical reaction of 1,2,7-thiadistannacycloheptane (6) in the presence of 2,3-dimethyl-1,3-butadiene

A deoxygenated THF (10 ml) solution of 1,2,7-thiadistannacycloheptane (**6**; 84 mg, 0.22 mmol) in the presence of 2,3-dimethyl-1,3-butadiene (0.3 ml, 2.65 mmol) was irradiated at room temperature for 4 h. The insoluble material was removed by filtration and the solvent was evaporated to give the mixture (89 mg) containing 1,3,5,2,4,6-trithiatristannin (**1**) and the recovered **6**. The residue was subjected to GPC to afford pure **1** (5 mg, conversion 15%) and **6** (12 mg, conversion 14%).

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