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Thermolysis, Photolysis, and Oxidation of an Overcrowded 1,3,2-Dithiastannetane Derivative

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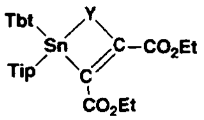
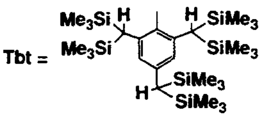
ABSTRACT

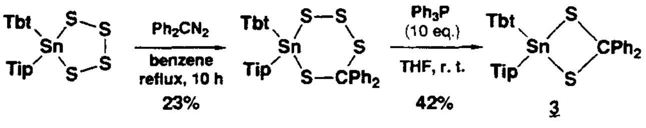
Reactions of a sterically crowded 1,3,2-dithiastannetane derivative bearing 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (=Tbt) and 2,4,6-triisopropylphenyl (=Tip) groups on the tin atom are described. Both thermolysis and photolysis of the 1,3,2,-dithiastannetane [Tbt(Tip)SnS$_2$CPh$_2$] resulted in the formation of products derived from the corresponding stannanethione [Tbt(Tip)Sn=S], while the oxidation reaction by m*-chloroperbenzoic acid gave a novel tin-containing heterocyclic system, an 1,2,4,5-oxadithiastannolane derivative.*



1 (Y=S)
2 (Y=Se)



Tip = 2,4,6-triisopropylphenyl



SCHEME 1

INTRODUCTION

The chemistry of small ring metallacycles of group 14 metals such as silicon, germanium, and tin has attracted much attention from the viewpoint of comparison with the corresponding strained carbocycles [1]. For example, we have recently succeeded in the synthesis of novel tin-containing four-membered ring systems, 1,2-chalcogenastannetes **1** and **2**, which are the first examples of tin-containing chalcogenete analogues, by taking advantage of a new and efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl (denoted as Tbt hereafter), and revealed their unique molecular structures by X-ray crystallographic analysis [2]. The successful isolation and noticeable stability of a novel class of small ring metallacycles **1** and **2** suggest that the bulky Tbt group effectively protects these highly strained molecules against their ring-opening reaction by nucleophiles. Furthermore, we have also reported the synthesis of a 1,3,2-dithiastannetane derivative **3** bearing Tbt and 2,4,6-triisopropylphenyl (denoted as Tip hereafter) on the tin atom starting from a novel tin-containing cyclic polysulfide, Tbt(Tip)SnS$_4$ [3]. In this article, we present some reactions of this overcrowded 1,3,2-dithiastannetane derivative **3** leading to the formation of interesting organotin compounds.

Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

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RESULTS AND DISCUSSION

When a mixture of 1,3,2-dithiastannetane **3** and an excess amount of 2,3-dimethyl-1,3-butadiene in toluene was heated at 120°C for 5 hours in a sealed tube, products **4–8** were obtained after chromatographic separation in yields as shown in Scheme 2. The six-membered ring products **4** and **8** are considered to be formed by the cycloaddition reaction of the butadiene with intermediary stannanethione **9** [4] and thiobenzophenone **10**, respectively, which are most likely produced by the thermal retro-cycloaddition of the dithiastannetane ring of **3**. While the mechanism for the formation of 1,2,4,3-trithiastannolane **6** is not clear at present, the formation of 1,3,2,4-dithiastannetane **5** and hydroxymercaptostannane **7** can be reasonably explained as the results of self-dimerization and hydrolysis of the intermediary stannanethione **9**, respectively. All the products here isolated were found to be identical with those obtained from the reactions of **9** generated by alternative synthetic methods [2,3].

Photolysis of dithiastannetane **3** in hexane was also performed to give **5**, probably derived from the intermediary stannanethione **9**, as depicted in Scheme 3, but most of **3** was recovered regardless of the light source, suggesting the existence of a photochemical pre-equilibrium between the starting material **3** and the thiones **9** and **10**.

Of particular note among the reactivities of an overcrowded dithiastannetane **3** is an oxidation reaction with a peracid. When **3** was treated with an equimolar amount of *m*-chloroperbenzoic acid (*m*CPBA) in dichloromethane at 0°C, 1,2,4,5-oxadithiastannolane 2-oxide **11** was isolated in 42% yield together with the recovery of **3** (44%) after chromatographic separation.

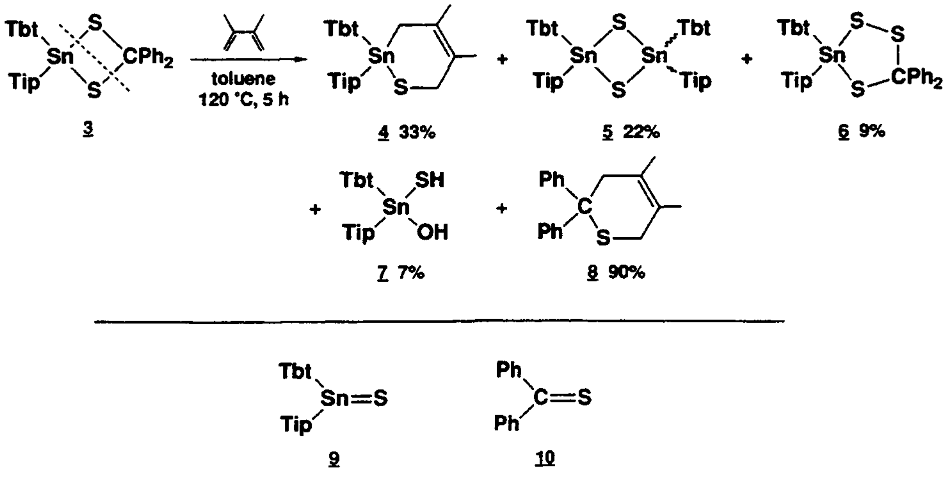
Since neither the sulfone nor the bis(sulfoxide) of **3** was obtained and almost half the amount of the starting material was recovered in this reaction, the formation of **11** can be interpreted in terms of the initial formation of sulfoxide **12** followed by the facile rearrangement leading to a ring-expanded oxadithiastannolane **13** and the successive oxidation of the sulfur atom in the position β to the Sn atom of **13**, which is sterically less hindered than that in the α-position. As for the stereochemistry of the sulfinyl group in **11**, the second molecule of *m*CPBA is considered to undergo stereospecific attack at the sulfur atom in a position β to the Sn atom of **13** from the less hindered direction, as illustrated in Scheme 4. The molecular geometry of **11** experimentally obtained by X-ray structural analysis (vide infra) and inspection of the CPK models dismissed the possibility that the oxidation takes place from the other direction. This reaction mechanism was further confirmed by the almost quantitative formation (86%; 98% conversion yield) of **11** in the oxidation of **3** using 2 equivalent moles of *m*CPBA under similar reaction conditions.

The molecular structure of the newly obtained tin-containing heterocyclic system **11** was satisfactorily confirmed by the spectral and analytical data and finally determined by X-ray crystallographic analysis. In Figure 1 is shown an ORTEP drawing of **11** together with its schematic views including the selected bond lengths and angles, which clearly indicate the cyclic sulfinic acid ester structure of **11**.

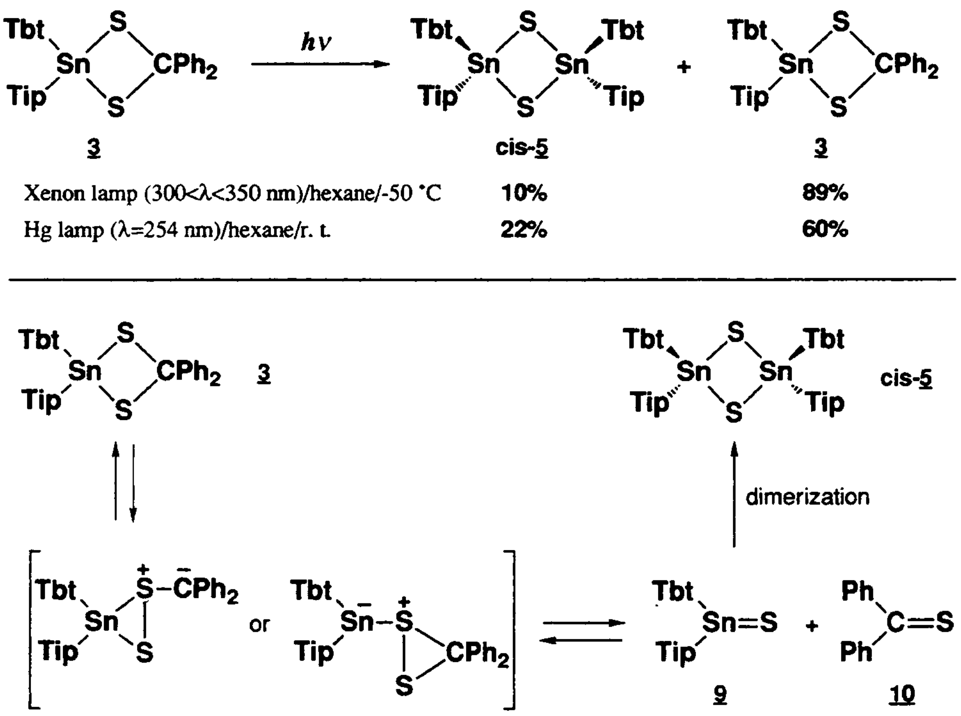
CONCLUSIONS

Some new reactivities of the overcrowded 1,3,2-dithiastannetane derivative **3** have been revealed, which reflect the remarkable bulkiness of the Tbt group. The formation of **11** in the oxidation of **3** should be noted as the first example of a 1,2,4,5-oxadithiastannolane ring system and is in sharp contrast to the ready formation of sulfone and bis

SCHEME 2

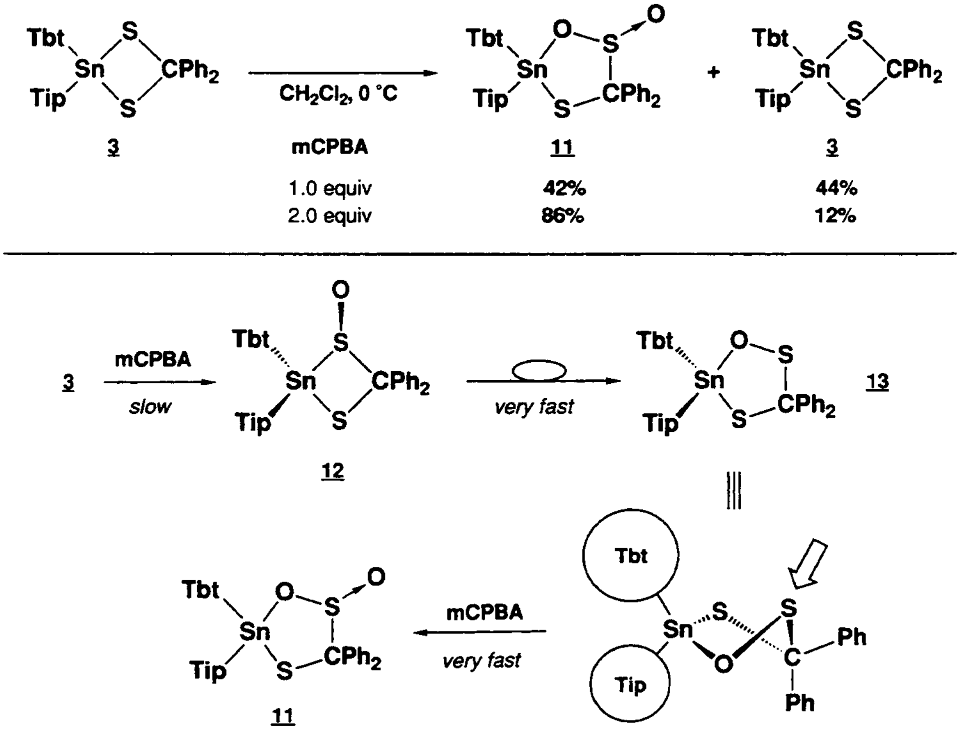


SCHEME 3



	cis-5	3
Xenon lamp (300<λ<350 nm)/hexane/-50 °C	10%	89%
Hg lamp (λ=254 nm)/hexane/r. t.	22%	60%

SCHEME 4



mCPBA	11	3
1.0 equiv	42%	44%
2.0 equiv	86%	12%

(sulfone) in the oxidation of the carbon analogous 1,3-dithietane derivative [5]. The high liability of the intermediary monosulfoxide **12** to ring expansion is most likely due to the ring strain caused by the bulky substituents and the higher affinity between tin and oxygen atoms than that between carbon and oxygen atoms.

Further investigation on the syntheses and reactions of the other small ring metallacycles containing group 14 metals is currently in progress.

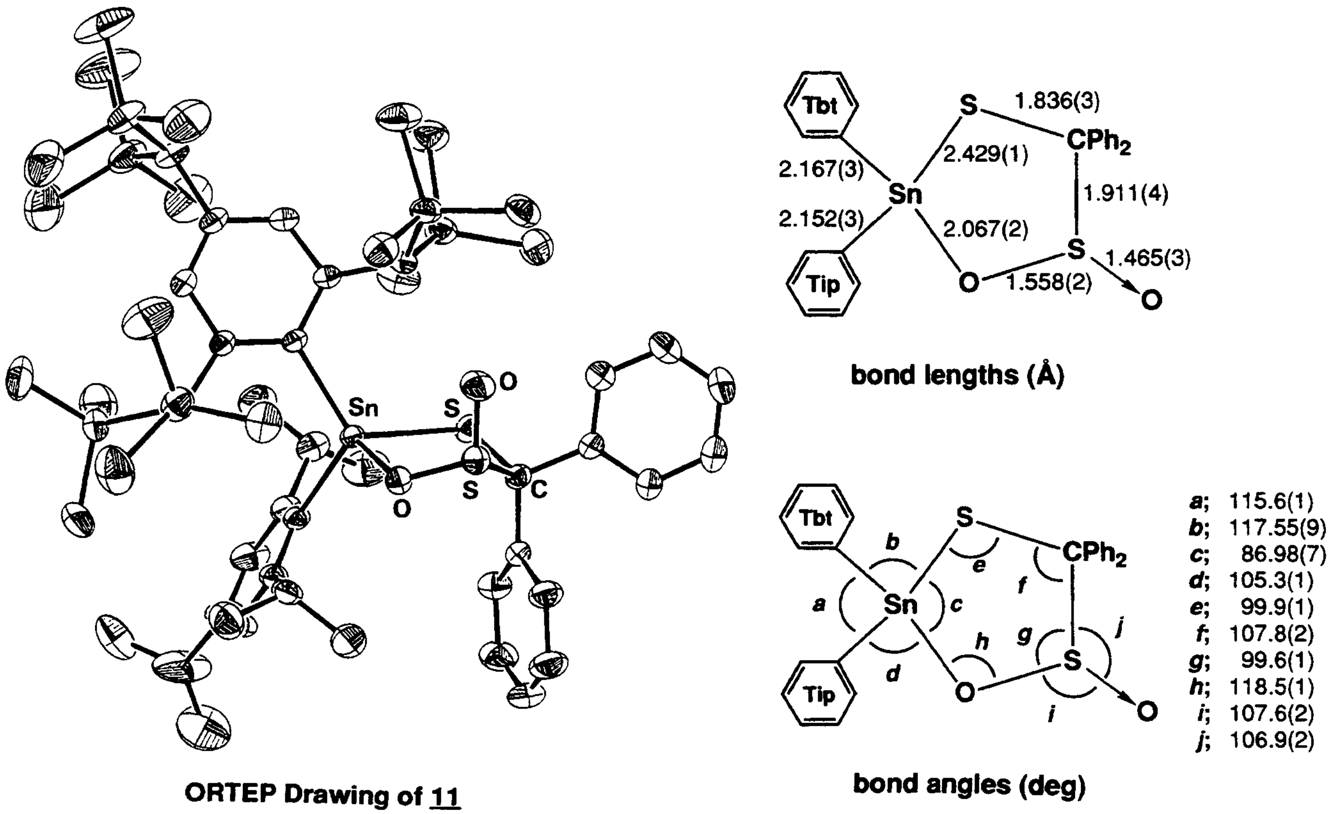
EXPERIMENTAL SECTION

General Procedure

All melting points were uncorrected. All solvents used in the reactions were purified by the reported methods. THF was purified by distillation from benzophenone ketyl before use. All reactions were carried out under an argon atmosphere unless otherwise noted. Preparative gel permeation liquid chromatography (GPLC) was performed by use of an LC-908 instrument with JAI gel 1H and 2H columns (Japan Analytical Industry, styrene-divinylbenzene copolymer, pore size 25 Å) with chloroform as solvent. Column chromatography was performed on silica gel (Wakogel C-200). Preparative thin layer chromatography (PTLC) was carried out with Merck Kieselgel 60 PF254 Art. 7747. The ^{1}H NMR spectra were measured in $CDCl_3$ with a Bruker AM-500 spectrometer using $CHCl_3$ as an internal standard. FABMS and high-resolution FABMS spectra were recorded on a JEOL SMX-102 mass spectrometer with *o*-nitorophenyl octyl ether as a matrix solvent.

Thermolysis of Dithiastannetane 3 *in the Presence of 2,3-Dimethyl-1,3-butadiene.*

A toluene solution (3 mL) of **3** [3b,c] (100 mg, 0.091 mmol) was heated at 120°C for 5 hours in a degassed sealed tube. After the solvent was evaporated, the residue was subjected to GPLC chromatography to give a fraction containing the Tbt-substituent (115 mg) and 2*H*-thiopyran derivative **8** (23 mg, 90%). The former fraction was purified with PTLC to afford 1,2-thiastannacyclohexene **4** (30 mg, 33%), 1,3,2,4-dithiadistannetane **5** (18 mg, 22%), 1,2,4,3-trithiastannolane **6** (9 mg, 9%), and hydroxymercaptostannane **7** (6 mg, 7%). Compound **5** was obtained as a mixture of *cis* and *trans* isomers, the molar ratio of which was found to be almost 1 : 1. The spectral and analytical data for **4–7** were identical with those we have previously re-



ORTEP Drawing of 11

bond lengths (Å)

bond angles (deg)

FIGURE 1 Molecular structure of **11**.

ported [3b,c]. The compound **8** was identified by comparison with the reported data [6].

Photolysis of Dithiastannetane 3

Irradiation with a Xenon Lamp. A solution of **3** (25.7 mg, 0.023 mmol) in 3 mL of hexane in a Pyrex glass tube was irradiated with a light of 300 < λ < 350 nm by a xenon lamp with a filter for 3 hours at −50°C. After removal of the solvent, the residue was separated by GPLC to afford cis-substituted 1,3,2,4-dithiadistannetane cis-**5** (2.2 mg, 10%) and the recovered **3** (22.9 mg, 89%). The spectral data of cis-**5** were identical with those we have previously reported [3c].

Irradiation with a Mercury Lamp. A solution of **3** (25.8 mg, 0.023 mmol) in 3 mL of hexane in a quartz cell was irradiated by a low pressure mercury lamp for 30 minutes at room temperature. After removal of the solvent, the residue was separated by GPLC to give cis-**5** (4.6 mg, 22%) together with the recovered **3** (15.5 mg, 60%).

Oxidation of Dithiastannetane 3

Reaction of **3** *with an Equimolar Amount of mCPBA.* A solution of **3** (50.6 mg, 0.046 mmol) in 10 mL of dichloromethane was cooled to 0°C. To this solution was added a dichloromethane solution (8 mL) of *m*CPBA (10.1 mg, 80% purity, 0.047 mmol) at the same temperature during 35 minutes. After evaporation of the solvent, the residue was separated by column chromatography (SiO_2/hexane:chloroform = 2:1) and PTLC (SiO_2/hexane:chloroform = 1:1) to afford 1,2,4,5-oxadithiastannolane 2-oxide **11** (23.1 mg, 42%) along with the recovered **3** (22.1 mg, 44%).

11: white crystals, mp 239–240°C (decomp). ^1H NMR ($CDCl_3$) δ 0.03 (s, 9H), 0.05 (s, 18H), 0.07 (s, 9H), 0.09 (s, 18H), 1.16 (br s, 12H), 1.26 (d, J = 6.9 Hz, 6H), 1.36 (s, 1H), 2.02 (s, 1H), 2.26 (s, 1H), 2.67 (sept, J = 6.6 Hz, 2H), 2.88 (sept, J = 6.9 Hz, 1H), 6.46 (s, 1H), 6.55 (s, 1H), 6.84–7.55 (m, 12H); IR(KBr) 1133 cm^{-1} ($\nu_{S=O}$); MS (FAB), m/z 1137 (MH^+, 0.7%), 1073 (2), 874 (20), 671 (41), 73 (100); high-resolution FABMS, obsd m/z 1137.4255; calcd for $C_{55}H_{93}O_2S_2Si_6{}^{120}Sn$ 1137.4312.

Reaction of **3** *with an Excess Amount of mCPBA.* To a dichloromethane solution (8 mL) of **3** (43.0 mg, 0.037 mmol) was added 16.0 mg (80% purity, 0.074 mmol) of *m*CPBA dissolved in 8 mL of dichloromethane at 0°C during 30 minutes. After removal of the solvent, the residue was chromatographed on PTLC (SiO_2/hexane:dichloromethane = 2.5:1) to give 38.0 mg (86%) of **11** together with the recovered **3** (5.3 mg, 12%). The conversion yield of **11** was 98%.

TABLE 1 Crystal and Intensity Collection Data for 1,2,4,5-Oxadithiastannolane 2-Oxide (**11**)

Mol formula	$C_{55}H_{92}O_2S_2Si_6Sn$
Mol weight	1136.65
Crystal system	*triclinic*
Space group	$P\bar{1}$
a, Å	12.651(2)
b, Å	25.608(4)
c, Å	10.611(2)
α, deg	90.51(2)
β, deg	108.48(2)
γ, deg	99.08(1)
V, $Å^3$	3213(2)
Z	2
D_{calcd}, g cm^{-3}	1.175
Crystal dimensions, mm	0.60 × 0.50 × 0.20
Linear absolute coefficient, cm^{-1}	6.04
Radiation	Mo K_α(λ = 0.71069 Å)
2θ range, deg	5–55
Scan type	ω
Total number of reflections scanned	15,491
Number of unique reflections	14,818
Number of observed reflections	9798 [$I > 3\sigma(I)$]
Number of variables	595
R	0.041
R_w	0.043
Residual electron density, e $Å^{-3}$	+0.84/−0.51

Single-Crystal X-ray Diffraction Analysis of 11 [7]

Single crystals of **11** suitable for X-ray diffraction analysis were grown by recrystallization from chloroform. All measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo $K\alpha$(λ = 0.71069 Å) radiation and use of a 12 KW rotating anode generator. Initial lattice parameters were determined from 25 accurately centered reflections with 2θ values in the range from 37° to 39°. Cell constants and other pertinent data were collected and are listed in Table 1. The intensity data were collected at 22 ± 1°C using the ω scan technique to a maximum 2θ value of 55.1°. Of the 15,491 reflections collected, 14,818 were unique (R_{int} = 0.024). The intensities of three representative reflections, which were measured after every 150 reflections, remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods [8]. The nonhydrogen atoms were refined anisotropically, while the hydrogen atoms were located in the calculated positions. The final cycle of full-matrix least-squares refinement was based on 9798 observed reflections [$I > 3.00\ \sigma(I)$] and 595 variable parameters and converged (largest parameter shift was

0.20 times its esd) with unweighted and weighted agreement factors of $R = 0.041$ and $R_w = 0.043$. All calculations were performed using the TEXSAN [9] crystallographic software package of Molecular Structure Corporation.

ACKNOWLEDGMENTS

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