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Chemistry of Heavy Carbene Analogues, R_2M (M = Si, Ge, Sn). 7.[1] A New and Convenient Source for Stannylenes, R_2Sn: 1,2-Bis(phenylthio)tetramethyldistannane, $Me_2(PhS)Sn-Sn(SPh)Me_2$

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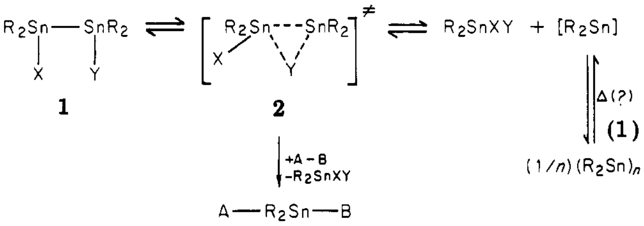
Stannylene extrusion/insertion equilibria, $R_2XSn-SnXR_2 \rightleftharpoons R_2SnX_2 + R_2Sn$, are found and investigated for X = Br and SPh. The Sn–Br and Sn–SPh bonds are efficient stannylene scavengers. $Me_2(PhS)Sn-Sn(SPh)Me_2$ is a convenient source both for thermal and photochemical stannylenoid reactions, giving 1,3,2-dioxastannolanes on reaction with 2 molar equiv of aldehyde or 1,3,2-dioxastannolenes by reaction with α-diketones such as α-naphthoquinone, biacetyl, or benzil. The saturated heterocycles can be converted by acetyl chloride to diacetates of glycols (under preservation of the D,L/meso relation). The unsaturated rings give diacetates of *Z* enediols.

Introduction

The chemistry of carbenes, R_2C, has been and still is a rapidly developing field. In this connection, during the last years, growing attention has been directed toward the heavier analogues, the silylenes, R_2Si,[3] germylenes, R_2Ge,[4] and stannylenes, R_2Sn.[5] These are of interest for synthetic purposes, and they also provide the opportunity to extend quantum chemical calculations to the heavier atoms of group 4[6] and to scrutinize the validity of the Woodward–Hoffmann rules of orbital symmetry for these elements and especially, for reactions of the heavy carbene analogues.[7]

Among known stannylene reactions, some proceed via a free stannylene, R_2Sn,[8] but others appear to take place via "stannylenoid mechanisms" (analogous to the "carbenoid mechanisms"[9]) in which a *free* stannylene does not appear to be involved.[5] Many of the thermal and the photochemical stannylene reactions of di- and polystannanes, 1, belong to this latter group with a transition state 2 being operative, e.g., for an insertion reaction shown in eq 1.



X = Y or X ≠ Y; X, Y = alkyl, Hal, OAc, SnR_3, $(-R_2Sn-)_n$

Apparently, the migratory aptitude of Y is important, in addition to the stability of R_2SnXY, for the usefulness of a stannylene source of this type. After some studies of the validity of eq 1 employing $Me_2BrSn-SnBrMe_2$, **1a**, we wish to report the use of a new and advantageous precursor for both thermal and photochemical stannylene transfer, 1,2-bis(phenylthio)tetramethyldistannane, **1b**.

Results and Discussion

(A) Thermal Behavior of 1a. $Me_2ClSn-SnClMe_2$ is a good source both for transfer of Me_2Sn and MeSnCl units

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(1) Part 6: see ref. 8.

(2) Scherping, K.-H. Dr. rer. nat. Thesis, University of Dortmund, 1981.

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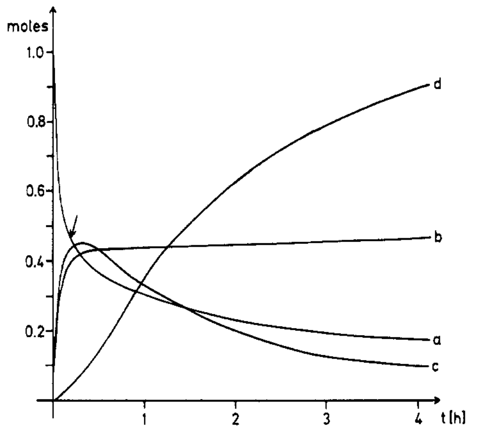


Figure 1. Thermolysis of $Me_2BrSn–SnBrMe_2$ (**1a**) at 80 °C in benzene: (a) **1a**; (b) Me_2SnBr_2; (c) $(1/n)(Me_2Sn)_n$; (d) Me_3SnBr (↑, observation of elemental tin).

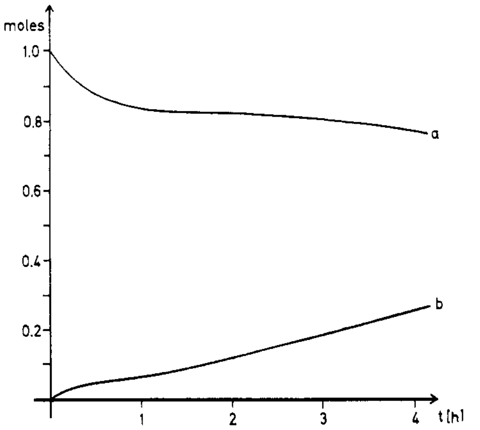
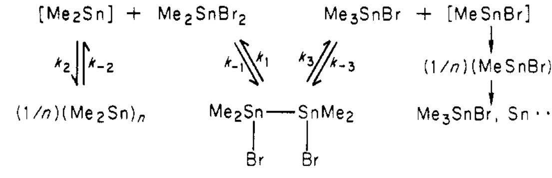


Figure 2. Thermolysis of $Me_2BrSn–SnBrMe_2$ (**1a**) at 80 °C in benzene: (a) **1a** in the presence of 5 molar equiv of Me_2SnBr_2; (b) Me_3SnBr under the same conditions.

to aldehydes and α-diketones.[10-13] Following our preliminary experience in the butyl series,[14] Br instead of Cl in 1 should be even more mobile with respect to eq 1. Thus, **1a** should be suited for a more thorough investigation of what really happens to a stannylene precursor of the type 1 during degradation.

At 80 °C in benzene, in absence of a reaction partner A–B for a stannylene, first a rapid decomposition of **1a** is observed with simultaneous formation of Me_2SnBr_2 and a stannylene oligomer, $(Me_2Sn)_n$. The ^1H NMR resonance (0.72 ppm) of the latter is very similar to that of the pure heptamer $(Me_2Sn)_7$, 0.64 ppm in toluene,[15] and excludes the presence of $Me_2BrSn–Me_2Sn–SnBrMe_2$ or the corresponding tetrastannane.[16] However, after 20 min, surprisingly, an equilibrium is reached (see Figure 1) which is subsequently altered slowly by the appearance of Me_3SnBr and elemental Sn. That there is really an equilibrium (k_1/k_{-1}) could be demonstrated by performing the thermolysis in the presence of 5 molar equiv of Me_2SnBr_2 (see Figure 2). About 85% of **1a** now is found in the equilibrium mixture. Therefore, eq 2 gives a full description of what is taking place. The following con-



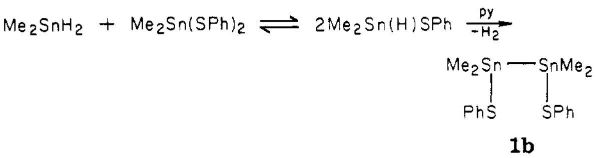
(2)

1a

clusions may be derived from this evidence. (a) **1a** is a rather good thermal stannylene Me_2Sn source, $k_1 \approx 10^{-3}$ s^{-1} at 80 °C. (b) Br is a good migrating group, Y (eq 1), probably passing transition state **2**. (c) Also Me is a migrating group, Y, but about 20 times slower than Br, $k_3 \approx 10^{-4}$ s^{-1}, passing probably transition state **2**, but with a bridged R group. (d) The Sn–Br bond is a powerful stannylene scavenger.[17] (e) The oligomer formation, surprisingly, is reversible, and $(Me_2Sn)_n$, thought to be thermally stable up to 150 °C,[18] releases easily the Me_2Sn units under these mild conditions, at least in the presence of Me_2SnBr_2.[19] Thus, eq 1 is, in principle, fully reversible. (f) Free radical reactions have very little, if anything, to do with the initial decay of **1a** since a large excess of *t*-BuBr, known to be a powerful scavenger for free stannyl radicals and methyl radicals as well, has only a very small effect on k_1. But, *t*-BuBr seems to react with (more or less) free Me_2Sn via the bulk equation $2\,t\text{-BuBr} + Me_2Sn \rightarrow Me_2SnBr_2 + 2\,t\text{-Bu}\cdot$, resulting in correspondingly higher concentrations of Me_2SnBr_2 and the nonappearance of the oligomer $(Me_2Sn)_n$.[20]

(B) Thermal and Photochemical Behavior of 1b. Halogen-containing distannanes, 1, as precursors for stannylenes have some drawbacks from practical use because of their sensitivity toward light and moisture. Accordingly, we sought other groups, *Y*, which do not have such problems and which exhibit a high "migratory aptitude" in the sense of eq 1. A promising group should be the thiophenyl substituent because sulfur in its ether forms undergoes easily complexation with higher coordination numbers, at least easier than the more electronegative oxygen.[21] As far as R is concerned, Me derivatives are decomposed easier than the corresponding Et- or Bu-substituted compounds.[10]

Therefore, we prepared the as yet unknown 1,2-bis(phenylthio)tetramethyldistannane, **1b**, following eq 3. The product forms colorless crystals, mp 89 °C, which are stable at room temperature in air, in the solid state, and in benzene solution as well and, therefore seems well suited for preparative purposes.



$$Me_2SnH_2 + Me_2Sn(SPh)_2 \rightleftharpoons 2Me_2Sn(H)SPh \xrightarrow[-H_2]{py} Me_2Sn(SPh)\text{—}Sn(SPh)Me_2 \quad (3)$$

1b

Thermolysis of **1b** at 80 °C in benzene is qualitatively similar to that of **1a** (Figure 1) but is more clear-cut in the quantitative sense. After rapid initial decay of **1b** to 40%

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[11] Grugel, Ch.; Neumann, W. P.; Sauer, J.; Seifert, P. *Tetrahedron Lett.* **1978**, 2847.

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[16] Derived from NMR data in: Gross, L.-W.; Moser, R.; Neumann, W. P.; Scherping, K.-H. *Tetrahedron Lett.* **1982**, *23*, 635, and unpublished results.

[17] The same applies to the Sn–Cl bond. Compare ref 16 and Moser, R. Dr. rer. nat. Thesis, University of Dortmund, 1980.

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[19] Mass spectrometry results indicate that $(Me_2Sn)_n$ generates Me_2Sn thermally even below 80 °C: Watta, B. Diploma Thesis, University of Dortmund, 1981.

[20] Detailed investigation is in progress.

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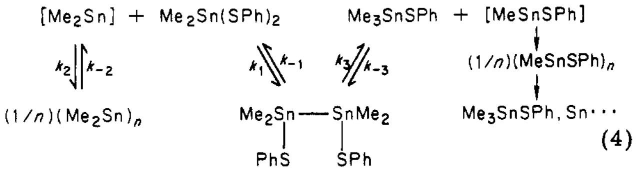
Table I. Yields and Stereochemistry of Dioxastannolanes 4 Synthesized Following Eq 5

R	*t*, h	% yield of 4	% of D,L isomer in 5
Me	6	91	60
Et	2	47	95
Pr	4	60	94
Ph	6	86	49

of the original value and appearance of the corresponding equivalents of Me$_2$Sn(SPh)$_2$ and (Me$_2$Sn)$_n$, for 4 h this equilibrium remains constant. Only afterward, was slow deposition of elemental tin observed and Me$_3$SnSPh appeared. Addition of 5 molar equiv of Me$_2$Sn(SPh)$_2$ shifts the equilibrium to 80% of **1b**. The decomposition of **1b** follows eq 4. Therefore, $k_1 \approx 10^{-3}$ s^{-1} and k_3 is of the order 5 × 10^{-5} s^{-1}. Thus, the migration (eq 1) of SPh is faster than that of Me. All the conclusions derived for **1a** (see above) are valid here, too, but SPh is a better thermal migrating group, Y, than is Br and migration of Me does not interfere during preparative applications. Thus, the Sn–SPh bond is found to be a new and effective stannylene scavenger.

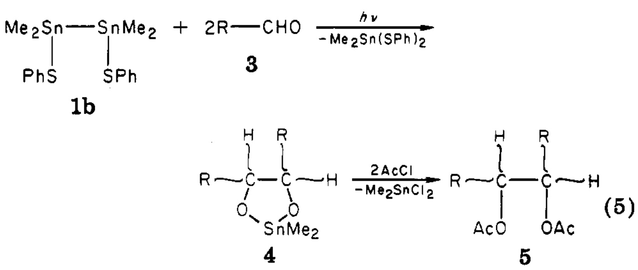


(4)

1b

Because of its long-waved UV absorption touching the visible, **1b** also should be a useful photolytic stannylene source. In Figure 3, the long-waved absorptions of several compounds, 1, X = Y = Cl, Br (**1a**), OAc, and SPh (**1b**), are compared for higher concentrations as are relevant for preparative applications, together with benzene as solvent and acetaldehyde as the standard reaction partner (see below). During photolysis of **1b** at 11 °C in benzene, the same substances appear and disappear as observed during thermolysis. Again, an excess of Me$_2$Sn(SPh)$_2$ shifts the equilibrium (k_1/k_{-1}) from 40% to 80% of **1b** as is expected. It remains constant for 4 h. Only then is a deposition of elemental tin observed. It can be hoped, therefore, that **1b** may be one of the most convenient stannylene sources for many preparative purposes, both thermally and photochemically.

(C) Thermal and Photochemical Application of 1b for Stannylene Reactions. Thermal stannylene additions to aldehydes and monoketones could not be achieved in many attempts and with various stannylene precursors.[10,12,22,23] This was confirmed by using **1b** and benzaldehyde. However, upon irradiation of **1b** with aldehydes smooth reductive coupling occurred, eq 5. The products, 1,3,2-dioxastannolanes, **4**, were isolated in higher yields and/or after shorter irradiation times than was possible when other Me$_2$Sn sources[10-13,22-24] were used; see Table I. The coproduct, Me$_2$Sn(SPh)$_2$, can be separated easily. For larger scale preparations, it may be recycled (eq 3).



1b **3**

(5)

4 **5**

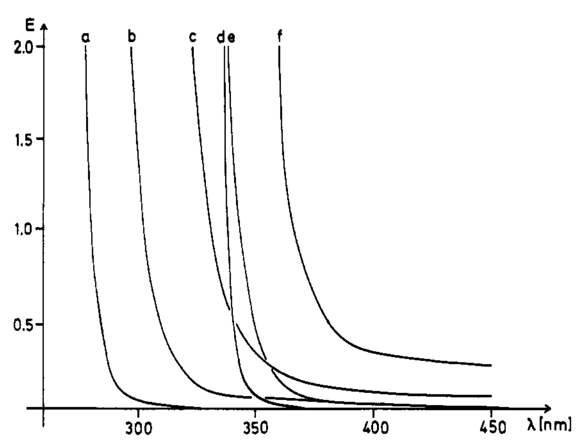
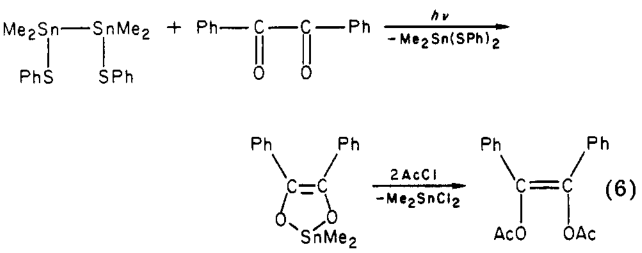


Figure 3. UV absorption spectra in preparative concentrations (*d* = 1 cm): (a) benzene, pure; (b) Me$_2$ClSn–SnClMe$_2$, 0.15 M in CH$_3$CN; (c) Me$_2$BrSn–SnBrMe$_2$, 0.15 M in CH$_3$CN; (d) acetaldehyde, 1.5 M in benzene; (e) Me$_2$(AcO)Sn–Sn(OAc)Me$_2$, 0.15 M in CH$_3$CN; (f) Me$_2$(PhS)Sn–Sn(SPh)Me$_2$, 0.15 M in CH$_3$CN.

Since dioxastannolanes with methyl substituents on the tin atom are practically insoluble, it still is an open question whether the simplest structure **4** is correct, or whether the product is polymeric. On the other hand, it could be demonstrated that the more soluble 2,2-diethyl-4,5-dimethyl-1,3,2-dioxastannolane is a monomer by determining the molecular weight by vapor pressure osmometry in benzene ($\sim 10^{-3}$ M).[13] In any case, derivatization with acetyl chloride yields the D,L/meso mixture of the corresponding glycol diacetate **5**, (Table I).

For comparison, the distannane Me$_2$(AcO)Sn–Sn(OAc)Me$_2$ with short-waved absorption (see Figure 3) was irradiated under the same conditions with acetaldehyde. Only a 27% yield of the dioxastannolane **4**, R = Me, was obtained, and this only after an irradiation time of 42 h. α-Diketones yield 1,3,2-dioxastannolenes via photochemical stannylenoid reactions.[12,13,23,24] In these cases, too, **1b** gave the best results obtained as yet. With benzil, a 72% yield of **6** could be isolated upon irradiation. Thermally, no reaction occurred at either 80 or 150 °C. The product **6** could be converted to the enediol diacetate **7**, as shown in eq 6, with preservation of the *Z* configuration. Apparently, the deeply yellow benzil absorbs most of the irradiation energy, giving probably the triplet. A detailed report of organotin photochemistry in the presence of carbonyl compounds will be published elsewhere.[25] Biacetyl, however, reacts only thermally (80 °C), giving a 71% yield



(6)

6 **7**

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(23) Sauer, J. Diploma Thesis, University of Dortmund, 1978.

(24) Neumann, W. P.; Schwarz, A. *Angew. Chem.* **1975**, *87*, 844; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 812.

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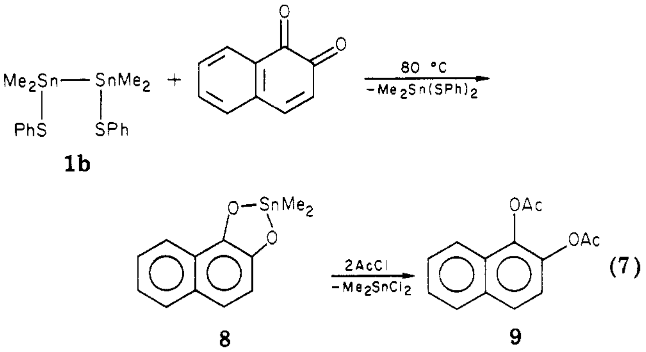
(26) Fieser, L. F. *J. Chem. Educ.* **1954**, *31*, 291.

of **6** (but Me instead of Ph), and not photochemically.

1,2-Naphthoquinone gives good yields (73%) of the naphthodiol derivative **8** in a thermal reaction. The latter can easily be converted into the diacetate **9**, eq 7.



1b

8

9

(7)

$Me_4Sn_2Cl_2$ also gives **8**, but in lower yield and with impurities.[12] With Et_5Sn_2Br as the stannylene source, **8** (Et instead of Me) has been prepared in good yield, but with impurities which are hard to separate,[12] and with Et_5Sn_2I at 20 °C the same Et derivative is obtained, but only in 44% yield. Again, **1b** may be recommended here with respect to yields and easy workup.

As mentioned, one must differentiate between a *free* stannylene mechanism and a concerted stannylenoid route. All observations during reactions 5, 6, and 7 concerning yields and reaction rate suggest that reactions of the stannylene precursor **1b** with carbonyl compounds take place via a stannylenoid mechanism, where the excited state **2** is complexed by the carbonyl compound.

Experimental Section

General Comments. All reactions were run under an argon atmosphere, because most of the organotin compounds used are sensitive to oxygen, especially the dibromodistannane **1a**. Photochemical procedures were carried out by using a 150-W high-pressure mercury lamp, TQ 150 Hanau, outside a quartz tube containing the reaction mixture. Temperature was maintained at 11 °C throughout the experiments: ^1H NMR, Varian EM-360 A, 60 MHz, chemical shifts in δ against Me_4Si. UV, Philips Unicam SP 1800; IR, Perkin-Elmer 457; mass spectra, Varian CH 5; elemental analysis, Heraeus CHN Monar.

Thermolysis of $Me_2BrSn-SnBrMe_2$, 1a. **1a** (62 mg, 0.14 mmol) and toluene (0.5 mmol, internal standard) were refluxed in benzene (5 mL). Decomposition of **1a** and formation of Me_2SnBr_2, Me_3SnBr, and $(Me_2Sn)_n$ were monitored by analyzing samples of the reaction mixture at specified time intervals by ^1H NMR (**1a**, 0.62, Me_2SnBr_2, 0.53, Me_3SnBr, 0.30, and $(Me_2Sn)_n$, 0.72 ppm). The same procedure was carried out by starting with **1a** and Me_2SnBr_2 (molar ratio 1:5).

Thermolysis of $Me_2(PhS)Sn-Sn(SPh)Me_2$, 1b. **1b** (504 mg, 0.976 mmol) and toluene (3.9 mmol, internal standard) were refluxed in benzene (4 mL). The procedure was the same as with **1a**: ^1H NMR **1b**, 0.34, $Me_2Sn(SPh)_2$, 0.19, Me_3SnSPh, 0.17 (estimation of the latter two products by ^1H NMR is not possible if one of them is present in large excess), and $(Me_2Sn)_n$, 0.47 ppm. The same procedure was carried out by starting with **1b** and $Me_2Sn(SPh)_2$ (molar ratio 1:5).

Photolysis of 1b. Same procedure as described for thermolysis of **1b** (see above) was used.

1,2-Bis(phenylthio)tetramethyldistannane, $Me_2(PhS)Sn-Sn(SPh)Me_2$, 1b. To $Me_2Sn(SPh)_2$ (18.35 g, 50 mmol) in diethyl ether (50 mL) at 20 °C was added Me_2SnH_2 (5.1 mL, 50 mmol). After addition of 10 drops of pyridine in the dark, the solution was stirred for 3 days (formation of H_2). After half of the ether had been evaporated, **1b** crystallized at -30 °C. The product was pure without recrystallization: yield, 17.2 g (66.8%); mp 89 °C; ^1H NMR (CH_2Cl_2) δ 0.44 (12 H, s, $^2J_{HSn}$ = 48.5–52 Hz, $^3J_{HSn}$ = 14 Hz, MeSn), 7.25 (10 H, m, Ph); MS (70 eV, 190 °C), *m/e* (relative intensities) 516 (M - 2H, 0.4%), 501 (M - Me - H, 4%), 368 (M - Me_2Sn, 31%), 274 (M - MeSnSPh, 8%), 259 (M/2, 100%). Anal. Calcd for $C_{16}H_{22}S_2Sn_2$: C, 37.3; H, 4.3. Found: C, 37.6; H, 4.4.

2,2,4,5-Tetramethyl-1,3,2-dioxastannolane, 4, R = Me. A solution of **1b** (3.22 g, 6.25 mmol) and acetaldehyde (3.52 mL, 62.5 mmol) in benzene (15 mL) was irradiated for 6 h. The precipitate was washed with benzene; recrystallization was not possible: yield 1.36 g (91.2%); mp 300 °C dec. Anal. Calcd for $C_6H_{14}O_2Sn$: C, 30.4; H, 6.0. Found: C, 30.9; H, 6.3.

Acetyl chloride was added dropwise to a suspension of **4** (R = Me) in benzene. The colorless solution was evaporated, and after addition of a little benzene it was analyzed by GC (4 m, OV 17): butane-2,3-diacetate (D,L/meso = 60:40) and Me_2SnCl_2.

The 1,3,2-dioxastannolanes **4** (R = Et, Pr, Ph) have been synthesized and analyzed corresponding to the procedure given above. (Since recrystallization also has been not possible, as mentioned above, elemental analysis gave poor results because of some SnO and R_2SnO that were admixed.)

2,2-Dimethyl-4,5-diethyl-1,3,2-dioxastannolane, 4, R = Et: yield 47%; mp 240 °C dec; MS (70 eV, 150 °C), *m/e* (relative intensities) 265 (M - H, 2%), 251 (M - Me, 1%), 237 (M - Et, 32%), 208 (M - 2Et, 74%), 193 (M - 2Et - Me, 95%), 135 (MeSn, 100%). Derivatization with acetyl chloride led to hexane-3,4-diacetate (D,L/meso = 94:5) and Me_2SnCl_2.

2,2-Dimethyl-4,5-dipropyl-1,3,2-dioxastannolane, 4, R = Pr: yield 60%; mp 203–205 °C. Derivatization with acetyl chloride led to octane-4,5-diacetate (D,L/meso = 94:6) and Me_2SnCl_2.

2,2-Dimethyl-4,5-diphenyl-1,3,2-dioxastannolane, 4, R = Ph: yield 86%, mp 270–272 °C dec. Derivatization with acetyl chloride led to 1,2-diphenylethane-1,2-diacetate (D,L/meso = 49:51) and Me_2SnCl_2.

2,2-Dimethyl-4,5-diphenyl-1,3,2-dioxastannolene, 6. A benzene (5-mL) solution of **1b** (0.72 g, 1.4 mmol) and benzil (0.88 g, 4.19 mmol) was irradiated for 20 h. The colorless precipitate was washed twice with *n*-hexane (1 mL). Recrystallization was not possible: yield 0.36 g (72%). Anal. Calcd for $C_{16}H_{16}O_2Sn$: C, 53.5; H, 4.4. Found: C, 52.6; H, 5.1. (The poor values are due to impurities mentioned above.) Derivatization with acetyl chloride as described above led only to (*Z*)-1,2-diphenylethylene-1,2-diacetate, **7**, whose IR spectrum was identical with that of an independently prepared sample,[26] and Me_2SnCl_2.

2,2-Dimethylnaphtho[2,1-*d*]-1,3,2-dioxastannolene, 8. When **1b** (0.60 g, 1.16 mmol) and 1,2-naphthoquinone (0.13 g, 0.81 mmol) in benzene (6 mL) were heated to 80 °C for 140 min, 0.18 g (73%) of **8** was formed. Recrystallization failed because of the insolubility of **8**; mp >300 °C. Anal. Calcd for $C_{12}H_{12}O_2Sn$: C, 47.0; H, 3.9. Found: C, 47.3; H, 4.0. Derivatization with acetyl chloride led exclusively to naphthalene-1,2-diacetate (GC) and Me_2SnCl_2.

Acknowledgment. We are grateful to the Minister für Wissenschaft und Forschung, Düsseldorf, and to the Fonds der Chemischen Industrie for support.

Registry No. **1a**, 65487-81-2; **1b**, 81987-77-1; **3** (R = Me), 75-07-0; **3** (R = Et), 123-38-6; **3** (R = Pr), 123-72-8; **3** (R = Ph), 100-52-7; **4** (R = Me), 81987-78-2; **4** (R = Et), 81987-79-3; **4** (R = Pr), 81987-80-6; **4** (R = Ph), 81987-81-7; **5** (R = Me) isomer 1, 22152-23-4; **5** (R = Me) isomer 2, 17998-02-6; **5** (R = Et) isomer 1, 81987-82-8; **5** (R = Et) isomer 2, 81987-83-9; **5** (R = Pr) isomer 1, 55668-11-6; **5** (R = Pr) isomer 2, 55668-12-7; **5** (R = Ph) isomer 1, 63435-67-6; **5** (R = Ph) isomer 2, 6316-82-1; **6**, 81987-84-0; **7**, 26431-43-6; **8**, 81987-85-1; **9**, 6336-79-4; $Me_2Sn(SPh)_2$, 4848-63-9; Me_2SnH_2, 2067-76-7; 1,2-naphthoquinone, 524-42-5.