A Convenient Preparation of 2,4,6-Trisubstituted 1,3,5-Triselenanes by Treating Aldehydes or Their Acetals with 2,2,4,4,6,6-Hexamethyl-1,3,5-triselena-2,4,6-tristannacyclohexane in the Presence of $BF_3 \cdot OEt_2$ and $AlCl_3$

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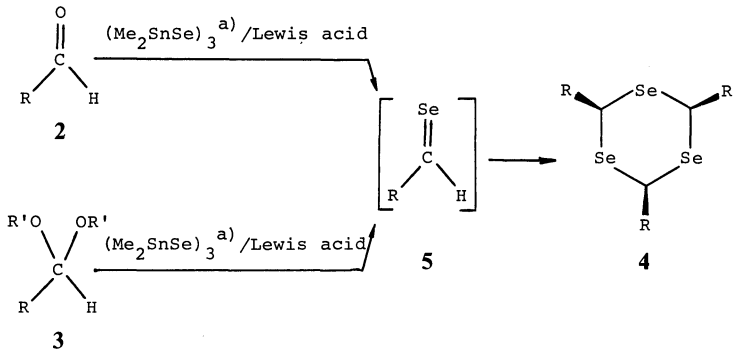
(Received March 30, 1992)

Synopsis. A convenient preparation of 2,4,6-trisubstituted 1,3,5-triselenanes was achieved by the treatment of aldehydes or their acetals with 2,2,4,4,6,6-hexamethyl-1,3,5-triselena-2,4,6-tristannacyclohexane, $(Me_2SnSe)_3$, in the presence of $BF_3 \cdot OEt_2$ and $AlCl_3$.

The efficient synthesis of selenium-containing heterocyclic compounds by using various selenating reagents related to H_2Se or Se^{2-} anion is of current interest in the field of organic heteroatom chemistry.[1-5] Among such reagents possessing reactive metal-selenium bonds, bis(trialkylstannyl) selenides have shown a milder selenating reactivity to the carbonyl group than those of the silicon analogues, due to the lower affinity to oxygen functionalities and the steric bulkiness of the trialkylstannyl groups.[6-8] It was supposed that the reactivities of 1,3,5-triselena-2,4,6-tristannacyclohexane would be enhanced by minimizing the steric bulkiness of the alkyl moieties. From such a standpoint, 2,2,4,4,6,6-hexamethyl-1,3,5-triselena-2,4,6-tristannacyclohexane **1**[9-15] was chosen as a tractable selenating reagent. In this paper we describe a new method used for a convenient preparation of 1,3,5-triselenanes **4**[16] by the treatment of aldehydes **2** or the corresponding acetals **3** with $(Me_2SnSe)_3$ **1** in the presence of $BF_3 \cdot OEt_2$ and $AlCl_3$.

The typical procedure is described regarding the preparation of 1,3,5-triselenane **4a** (R=Ph). To a CH_2Cl_2 solution of benzaldehyde ethylene acetal **3a** (R=Ph) was added 0.33 equiv of **1**, 2 equiv of $BF_3 \cdot OEt_2$, and 0.7 equiv of $AlCl_3$. The reaction mixture was stirred at 0 °C (1 h) to room temperature (4 h) under an N_2 atmosphere. After the usual work-up and subsequent recrystallization of the crude products from $CHCl_3$, 2,4,6-triphenyl-1,3,5-triselenane **4a** (R=Ph) was

Table 1. Preparation of 2,4,6-Trisubstituted 1,3,5-Triselenanes **4** Using $(Me_2SnSe)_3$ **1**



R	R′		Lewis acid/equiv		Conditions	Yield/% of **4**
			$BF_3 \cdot OEt_2$	$AlCl_3$		
C_6H_5	—	(**2a**)	2	—	r.t./56 h	54
C_6H_5	—	(**2a**)	—	1.7	0 °C/1 h→r.t./3 h	Trace
C_6H_5	—	(**2a**)	1	0.7	0 °C/2 h→r.t./11 h	56
C_6H_5	$-(CH_2)_2-$	(**3a**)	3	—	r.t./20 h	75
C_6H_5	$-(CH_2)_2-$	(**3a**)	—	2	0 °C/1 h→r.t./3 h	9[b]
C_6H_5	$-(CH_2)_2-$	(**3a**)	2	0.7	0 °C/1 h→r.t./4 h	90
4-CH_3O-C_6H_4	—	(**2b**)	1	0.35	0 °C/1 h→r.t./56 h	35
4-CH_3-C_6H_4	—	(**2c**)	1	0.35	0 °C/1 h→r.t./23 h	47
4-CH_3-C_6H_4	$-(CH_2)_2-$	(**3c**)	2	0.53	0 °C/1 h→r.t./5 h	79
4-Cl-C_6H_4	—	(**2d**)	1	0.35	0 °C/1 h→r.t./30 h	7
4-Cl-C_6H_4	$-(CH_2)_2-$	(**3d**)	2	0.53	0 °C/1 h→r.t./5 h	74
CH_3	—	(**2e**)	1	0.7	0 °C/1 h→r.t./9 h	79
CH_3	CH_3	(**3e**)	2	0.7	0 °C/1 h→r.t./3 h	83

a) 0.34 equiv of $(Me_2SnSe)_3$ **1** was used. b) In this case, benzaldehyde was obtained in 51% yield.

obtained as stable colorless needles in 90% yield. The resulting compound **4a** was completely identical in all respects with the reported physical properties.[5,16] Conversion of various aldehydes and their acetals possessing aromatic and aliphatic substituents to the corresponding 1,3,5-triselenanes was also achieved in a similar manner. Interestingly, 1,3,5-triselenanes **4**, possessing electron donating substituents on the benzene rings, formed 1 : 1 adducts[5] with $CHCl_3$, and the $CHCl_3$ was easily removed by heating to 130 °C for a few hours in vacuo, except for the case of the **4b** · $CHCl_3$ adduct. These results are given in Table 1.

Several features of the selenating reaction using reagent **1** were revealed as shown below. The preparations of 1,3,5-Triselenanes **4** were achieved more efficiently from acetals **3** than from the original aldehydes **2**. It can thus be seen from these results that the higher affinity of acetal oxygen atoms to Lewis acids in acetals **3** was advantageous for preparing 1,3,5-triselenanes. However, it was interesting that a single Lewis acid was not sufficiently effective to accelerate the reaction. When $BF_3 \cdot OEt_2$ was used as the Lewis acid in the reaction system, the time required to complete the reaction was prolonged. The corresponding aldehydes were recovered in all cases. An alternative use of $AlCl_3$ in the reaction of acetals **3** with reagent **1** also afforded aldehydes **2**, mainly in addition to a small amount of unidentified materials. In contrast, a combined treatment with $AlCl_3$ and $BF_3 \cdot OEt_2$ gave good results. When aldehyde **2a** (R=Ph) was treated with reagent **1** in the presence of $BF_3 \cdot OEt_2$ (1 equiv) and $AlCl_3$ (0.7 equiv), the yield of **4a** (R=Ph) rose to 56%. The best result was obtained (90% yield) when the reaction was carried out by treating acetal **3a** with reagent **1** in the presence of $BF_3 \cdot OEt_2$ and $AlCl_3$. However, details concerning the reaction mechanism are still uncertain.[17]

Trapping of precursors of 1,3,5-triselenane **4a** was carried out by treating acetal **3a** with reagent **1**, $BF_3 \cdot OEt_2$, and $AlCl_3$ in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene to form 2-phenyl-5,6-dihydro-2*H*-selenin **6a** in 50% yield. In contrast, no [4+2] cycloadduct **6a** was obtained when **4a** was treated with an excess amount of diene in the presence of these Lewis acids.[18] These results clearly showed that selenoaldehydes **5** were generated transiently during the primary stage of the reaction, and that there was little possibility of a Lewis acid-induced ring cleavage of **4a**.

Conclusively, the present work demonstrated a novel utility of reagent **1** for the efficient and convenient syntheses of 1,3,5-triselenanes **4**. Applications of reagent **1** to organic syntheses as well as the further transformations of compounds **4** to various cyclic polyselenides are in progress in our laboratory.

Experimental

Materials. All acetals were prepared from aldehydes by the usual method. The reagents, including Me_2SnCl_2, $BF_3 \cdot OEt_2$, $AlCl_3$, and 2,3-dimethyl-1,3-butadiene, were commercial reagent-grade materials and were purified by recrystallization, distillation, or by sublimation before use. Commercially available $NaBH_4$ and elemental selenium were also used. All of the solvents were dried with an appropriate drying agent and freshly distilled before use.

Instruments. The IR spectra were recorded with a JASCO FT/IR-7300 infrared spectrophotometer. ^1H NMR spectra were recorded with a Hitachi R-22 (90 MHz) spectrometer in a $CDCl_3$ solution containing tetramethylsilane (TMS) as an internal standard. MS spectra were recorded with a Hitachi M-2000 spectrometer, with a direct inlet system operating at 20 or 70 eV. Elemental analyses were performed with a Yanagimoto MT-3 CHN Analyzer.

Preparation of 2,2,4,4,6,6-Hexamethyl-1,3,5-triselena-2,4,6-tristannacyclohexane 1. To a stirred mixture of selenium powder (11.5 g, 146 mmol) and 125 ml of distilled water in a three-necked flask under an N_2 atmosphere at 0 °C, $NaBH_4$ (11.6 g, 307 mmol) was gradually added. An aqueous solution of Me_2SnCl_2 (35.4 g, 161 mmol) was then added dropwise to the reaction mixture. The reaction mixture was stirred at room temperature for 1 h and was extracted with CH_2Cl_2. The organic layer was washed twice with water and dried over anhydrous Na_2SO_4, followed by concentration to afford a grayish solid. Recrystallization of the crude product from methanol allowed us to isolate **1** (29.4 g, 43.1 mmol) in 87% yield as colorless plates.[9,10]

General Procedure for the Reactions of Aldehydes or Their Acetals with Reagent 1. To a CH_2Cl_2 solution of $(Me_2SnSe)_3$ **1** (500 mg, 0.732 mmol) and benzaldehyde ethylene acetal **3a** (341 mg, 2.27 mmol) was added a 20 ml CH_2Cl_2 solution of $BF_3 \cdot OEt_2$ (686 mg, 4.83 mmol) and powdered $AlCl_3$ (199 mg, 1.49 mmol). The reaction mixture was stirred under an N_2 atmosphere at 0 °C for 2 h and at room temperature for 11 h. After treating with an aqueous $NaHCO_3$ solution the reaction mixture was extracted with CH_2Cl_2. The organic layer was washed with water and dried over anhydrous Na_2SO_4. A crude yellow solid was obtained (428 mg) upon removing the solvent. Recrystallization of the crude product from $CHCl_3$ afforded 1,3,5-triselenane **4a**[5,16] (207 mg) in 90% yield as colorless needles.

The treatment of *p*-anisaldehyde **2b** and *p*-tolualdehyde ethylene acetal **3c** with $(Me_2SnSe)_3$ and $BF_3 \cdot OEt_2$–$AlCl_3$ in CH_2Cl_2 followed by recrystallization from $CHCl_3$ gave the corresponding 1 : 1 $CHCl_3$ adduct of 1,3,5-triselenanes **4b** and **4c** in 35 and 79% yields, respectively. The latter product was heated to 130 °C for 5 h in vacuo to afford 1,3,5-triselenane **4c** in quantitative yield.

2,4,6-Triphenyl-1,3,5-triselenane (4a): Colorless needles, mp 189 °C (decomp), (lit,[5,16] 189 °C).

2,4,6-Tris(4-methoxyphenyl)-1,3,5-triselenane (4b) · $CHCl_3$: Colorless needles, mp 155—156 °C (decomp); MS (*m/z*) 200 (M^+− $CHCl_3$/3, 61%, ^{80}Se); IR (KBr) 2835, 1607, 1508, 1251, 1030, 835, 735, 655 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.78 (9H,s), 5.46 (3H,s), 6.83 (6H, d, *J*=9 Hz), 7.34 (6H, d, *J*=9 Hz). Found: C, 42.30; H, 3.53%. Calcd for $C_{24}H_{24}O_3Se_3 \cdot CHCl_3$: C, 41.90; H, 3.52%.

2,4,6-Tris(4-methylphenyl)-1,3,5-triselenane (4c) · $CHCl_3$: Colorless needles, mp 189 °C (decomp); MS (*m/z*) 184 (M^+−$CHCl_3$/3, 92%, ^{80}Se); IR (KBr) 2927, 1610, 1509, 1213, 1144, 1018, 824, 758, 724, 672 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.34 (9H,s), 5.55 (3H, s), 7.19 (6H, d, *J*=8 Hz), 7.31 (6H, d, *J*=8 Hz). Found: C, 44.84; H, 3.74%. Calcd for $C_{24}H_{24}Se_3 \cdot CHCl_3$: C, 44.90; H, 3.77%. **4c**: IR (KBr) 2920, 1611, 1509, 1214, 1144, 1019, 825, 758, 725, 672 cm^{-1}. Found: C, 52.41; H, 4.43%. Calcd for $C_{24}H_{24}Se_3$: C, 52.48; H, 4.40%.

2,4,6-Tris(4-chlorophenyl)-1,3,5-triselenane (4d): Colorless needles, mp 184—185 °C (decomp); MS (*m/z*) 206 (M^+/3, 60%, ^{80}Se); IR (KBr) 2900, 2300, 1890, 1476, 1400, 1210, 1140, 1080, 1010, 820, 720, 640 cm^{-1}; ^1H NMR ($CDCl_3$) δ=5.51 (3H, s), 7.34 (12H, s). Found: C, 41.15; H, 2.47%. Calcd for $C_{21}H_{15}Cl_3Se_3$: C, 41.31; H, 2.48%.

2,4,6-Trimethyl-1,3,5-triselenane (4e):[1] Colorless needles, mp 59.0—78.0 °C (inseparable mixture of α- and β-isomer,

$\alpha:\beta$=3:2); MS (*m/z*) 324 (M^+, 21%, ^{80}Se), 108 ($M^+/3$, 4%, ^{80}Se); IR (KBr) 2948, 1436, 1370, 1153, 1027, 960, 629 cm^{-1}; ^1H NMR ($CDCl_3$) α-isomer, δ=1.80 (6H, d, *J*=7 Hz), 2.09 (3H, d, *J*=7 Hz), 4.57 (1H, q, *J*=7 Hz), 4.69 (1H, q, *J*=7 Hz); β-isomer, δ=1.82 (9H, d, *J*=7 Hz), 4.35 (3H, q, *J*=7 Hz). Found: C, 22.51; H, 3.76%. Calcd for $C_6H_{12}Se_3$: C, 22.45; H, 3.77%.

Trapping of Selenobenzaldehyde 5a by 2,3-Dimethyl-1,3-butadiene. To a 20 ml CH_2Cl_2 solution of $(Me_2SnSe)_3$ **1** (232 mg, 0.34 mmol), benzaldehyde ethylene acetal **3a** (150 mg, 1.0 mmol), and an excess amount of 2,3-dimethyl-1,3-butadiene was added $BF_3\cdot OEt_2$ (284 mg, 2.0 mmol) and $AlCl_3$ (23 mg, 0.17 mmol). The reaction mixture was stirred at room temperature for 20 h. After the usual work-up and chromatographic separation, 2-phenyl-5,6-dihydro-2*H*-selenin **6a**[16] was isolated in 50% yield as a colorless oil.

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17) No changing of ^1H NMR chemical shift of the methyl group (δ=1.00) was observed by adding $BF_3\cdot OEt_2$, $AlCl_3$, or both of the Lewis acids to the $CDCl_3$ solution of $(Me_2SnSe)_3$. TLC monitoring also showed that $(Me_2SnSe)_3$ remained unchanged by the treatment of these Lewis acids. From these results, the mechanism involving the generation of Al_2Se_3 and Me_2SnCl_2 was clearly excluded out.
18) Soft Lewis acid such as $SnCl_4$ was effective for the retro [2+2+2] type ring cleavage of 1,3,5-triselenanes **4** to generate selenoaldehydes **5**.[16]