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Stannic Chloride-Induced Unsymmetrical C–Se Bond Cleavage of Bis(*N*,*N*-dimethylcarbamoylseleno)methanes: Novel Generation of Selenoaldehydes

Yaling Gong, Kazuaki Shimada, Hidenori Nakamura, Masamichi Fujiyama, Akihiro Kodama, Miyuki Otsuki, Rei Matsumoto, Shigenobu Aoyagi, and Yuji Takikawa

Department of Chemical Engineering, Faculty of Engineering, Iwate University, Morioka, Iwate 020-8551, Japan

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ABSTRACT: *Treatment of bis(N,N-dimethylcarbamoylseleno)methanes with $SnCl_4$ afforded β-1,3,5-triselenanes in moderate to high yields, and the key intermediates of the reactions, i.e., acylselonium ions and selenoaldehydes, were successfully trapped by using allyltrimethylsilane or 2,3-dimethyl-1,3-butadiene to obtain the allylation products or the cycloadducts, respectively.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:125–135, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20190

INTRODUCTION

Recently, various methodologies for the generation of selenoaldehydes **3** have been reported in the light of their structural interests, their potentiality as new reactive intermediates for the organic reactions, and the increasing interests in the biological activities [1–3] for some selenoaldehydes. The synthetic methodologies for selenoaldehydes **3** are roughly classified to the five categories, i.e., (i) oxygen–selenium exchanging reactions of aldehydes [4–13], (ii) direct selenation of intermediary carbenes or carbenoids using elemental selenium [14–16], (iii) sigmatropic rearrangement of substituted alkenyl selenides [17], (iv) elimination of selenides bearing a suitable leaving group adjacent to the selenium atom [18–21], and (v) alkylation of stable selenoformate esters [22–25]. Most methods required multistep processes to prepare the suitable precursors for selenoaldehydes **3**, and these problems just prompted us to the new-type generation of selenoaldehydes **3** through fragmentation of easily preparable symmetrical diselenoacetals. However, to date, conversion of symmetrical diseleno- or ditelluroacetals into the corresponding chalcogenoaldehydes or chalcogenoketones was not studied at all due to the lack of preparative method of such precursors bearing a suitable chalcogen-protecting group on each chalcogen atoms in spite of their potent synthetic convenience. In the course of our studies on the novel generation of highly reactive species related to higher row chalcogenocarbonyl compounds, we previously reported a convenient

Correspondence to: Kazuaki Shimada; e-mail: shimada@iwate-u.ac.jp.
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preparation of stable ditelluroacetal derivatives **2** using the reaction of *N*,*N*-dimethyltellurocarbamate ions with *gem*-dihaloalkanes [17,26]. These results urged us to the preparation of symmetrical diselenoacetals **1** and the further reactions of **1** with a Lewis acid on the basis of the coordinating interaction between the selenocarbamate moiety and a soft Lewis acid [27]. Actually, diselenoacetals **1**, bearing a removable *N*,*N*-dimethylcarbamoyl group on each selenium atoms, are just expected to undergo Lewis acid induced unsymmetrical C—Se bond cleavage to generate selenoaldehydes **3** via acylselonium ions **A** through a push–pull type elimination of *N*,*N*-dimethylselenocarbamate ion and *N*,*N*-dimethylcarbamoyl cation [28]. According to our expectation as mentioned above, we started our exploration on the reaction of diselenoacetals **1** with a soft Lewis acid, i.e., $SnCl_4$, in the presence or absence of trapping agents, and we just found a new and convenient method for generation of selenoaldehydes **3** through the reaction of **1** with $SnCl_4$ under mild conditions as well as a novel stepwise fragmentation of **1** involving the in situ formation of key intermediates **A** as the actual precursors of **3** [29]. In this paper, we describe a full account on the new and convenient method for generation of selenoaldehydes **3** starting from symmetrical diselenoacetals **1**.

RESULTS AND DISCUSSION

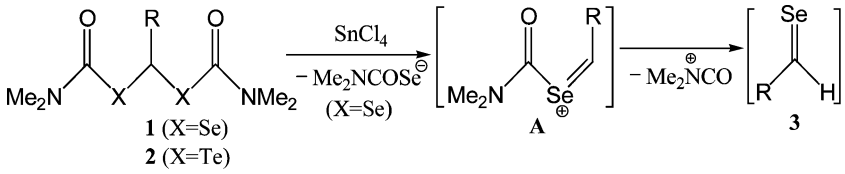
Stepwise Preparation of Bis(N,N-dimethylcarbamoylseleno)methanes **1** *Starting from Bis-(N,N-Dimethylcarbamoyl) Diselenide* **4**

Bis(*N*,*N*-dimethylcarbamoyl) diselenide **4** [30] was at first prepared by treating dry *N*,*N*-dimethylformamide (DMF), sodium metal, and elemental selenium at 100–110°C followed by aerobic exposure at RT according to the previous reports [31]. Subsequently, stepwise treatment of a DMF solution of diselenide **4** with NaH [31,32] and a *gem*-dihaloalkane **5** (benzal bromide **5a**, *m*-chlorobenzal bromide **5b**, *p*-chlorobenzal bromide **5c**, 1,1-dibromoethane **5d**, dibromomethane **5e**, and ethyl dichloroacetate **5f**, respectively) efficiently afforded air-stable bis(*N*,*N*-dimethylcarbamoylseleno)methanes **1a–f** [26], which are regarded as a new class of symmetrical diselenoacetals bearing a *N*,*N*-dimethylcarbamoyl group on each selenium atoms. On the other hand, stepwise treatment of **4** with $NaBH_4$ with **5a** in a mixed solvent of C_2H_5OH–DMF (1:1) only gave **1a** in 20% yield along with the formation of dibenzyl diselenide as a major product [31], and the use of diisobutylaluminum hydride (DIBAH), in place of NaH, also gave discourageous results. All the results are shown in Table 1.

Compounds **1** are expected to undergo unprecedented push–pull type stepwise fragmentation involving elimination of selenocarbamate ion and acyl cation through the coordinating interaction with a soft Lewis acid.

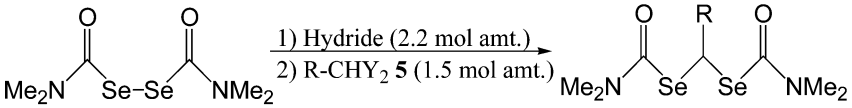
Formation of β-1,3,5-Triselenanes **6** *by Treating Diselenoacetals* **1** *with* $SnCl_4$

Treating a dichloromethane, a chloroform, or a benzene solution of **1a–f** with TsOH or a hard Lewis acid, such as $BF_3{\cdot}OEt_2$ and $TiCl_4$, resulted in quantitative recovery of **1** in all cases. On the other hand, as expected, treatment of **1a–d** with $SnCl_4$ (2.0 mol amt.) at RT under an Ar atmosphere afforded β-1,3,5-triselenanes **6a–d** [6,10,33–35], the trimers of selenoaldehydes **3a–d**, as the major products along with **4** and the recovery of **1**. The yields of **6a–d** were efficiently improved by the use of 3.0–5.0 molar amount of $SnCl_4$, and in such cases neither the stereoisomers of **6a–d** nor any other bypoducts, except for trace amounts of **4** and aldehydes **7**, were found in the crude products. In contrast, **1e** and **1f** were not reactive toward $SnCl_4$ under the similar mild reaction condition. Interestingly, a similar treatment of **1a** with $SnCl_4$ under an aerobic condition just gave benzaldehyde **7a** as a main product besides **4**. All the results are shown in Table 2.



Interestingly, treatment of a chloroform solution of **1a** with $SnCl_4$ at refluxing temperature afforded an epimeric mixture of 1,2,4-triselenolanes **8a** (10%, approximately 1:1 mixture) [36–39] along with the formation of selenocarbamate **9a** (25%), diselenide **4** (14%), and a trace amount of **6a**. A similar reaction of a chloroform solution of **1e** with $SnCl_4$ at

TABLE 1 Preparation of Bis(*N,N*-dimethylcarbamoylseleno)methanes **1**

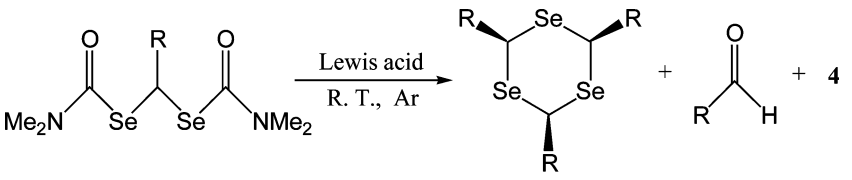


4 **1**

		gem-Dihaloalkane **5**				
Hydride	*Solvent*	*R*	*Y*	*Temperature (°C)*	*Time (h)*	*Yield (%)* **1**
$NaBH_4$	EtOH–DMF (1:1)[a]	C_6H_5	Br	RT	6	20 (**1a**)[b]
NaH	DMF[c]	C_6H_5	Br	RT	11	62 (**1a**)
NaH	DMF[c]	*m*-ClC_6H_4	Br	RT	9	51 (**1b**)
NaH	DMF[c]	*p*-ClC_6H_4	Br	RT	15	35 (**1c**)
NaH	DMF[c]	CH_3	Br	RT	14	59 (**1d**)
NaH	DMF[c]	H	Br	RT	2	65 (**1e**)
NaH	DMF[c]	$CO_2C_2H_5$	Cl	80	72	46 (**1f**)

[a]Condition: −50°C to 0°C for 30 min.
[b]Dibenzyl diselenide was formed in 65% yield.
[c]Condition: 0°C for 2 h.

TABLE 2 $SnCl_4$-Induced Conversion of Bis(*N,N*-dimethylcarbamoylseleno)methanes **1** into β-1,3,5-Triselenanes **6**



1 **6** **7**

Substrate **1**				*Yield (%)*			
R	*Lewis Acid (mol amt.)*	*Solvent*	*Time (h)*	**6**	**7**	**4**	*Recovery*
C_6H_5 (**1a**)	$BF_3{\cdot}OEt_2$ (2.0)	CH_2Cl_2	1	0	0	0	Quant.
C_6H_5 (**1a**)	$SnCl_4$ (3.0)	CH_2Cl_2	1	58 (**6a**)[a]	Trace (**7a**)	16	Trace
m-ClC_6H_4 (**1b**)	$SnCl_4$ (5.0)	Benzene	6	91 (**6b**)	Trace (**7b**)	Trace	Trace
p-ClC_6H_4 (**1c**)	$SnCl_4$ (5.0)	Benzene	6	83 (**6c**)	Trace (**7c**)	Trace	Trace
CH_3 (**1d**)	$SnCl_4$ (5.0)	CH_2Cl_2	24	46 (**6d**)	0[b]	4	0
H (**1e**)	$SnCl_4$ (5.0)	Benzene	6	0	0	0	Quant.
$CO_2C_2H_5$ (**1f**)	$SnCl_4$ (5.0)	Benzene	6	0	0	0	Quant.

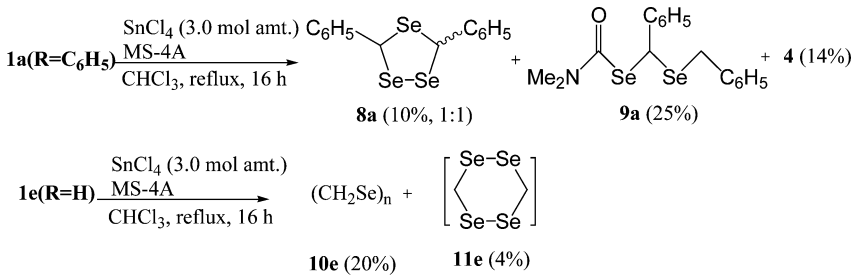
[a]References [6,10,33–35].
[b]Acetaldehyde **7d** was not found or detected at all in the crude mixture may be due to evaporation during the workup procedure.

refluxing temperature just gave a small amount of solvent-insoluble polymeric compound, characterizable to be polymethylene selenide (**10e**, approximately 20%) [40–47] by using IR spectrum, along with an unstable compound characterized by novel 1,2,4,5-tetraselenane (**11e**, approximately 4%). The similar reaction of **1f** at refluxing temperature just gave a complex mixture.

It was assumed that novel cyclic polyselenides, **8** and **11**, and polymethylene selenide **10e** were formed through an aerobic oxidation of **6** in the presence of Lewis acid. However, the formation pathway of these products remained unclear at this time (Scheme 1).

NMR Monitoring of the Reaction of Bis(N,N-dimethylcarbamoylseleno)phenylmethane **1a** *with* $SnCl_4$

When a $CDCl_3$ solution of **1a** was treated with $SnCl_4$ (0.5 mol amt.) in an NMR tube at 25°C, the signals of the ^1H NMR spectrum of the reaction mixture revealed a slight downfield shift with the complete retaining of their original symmetrical spectral pattern involving a pair of singlets assigned to the *N,N*-dimethylcarbamoyl groups. Further addition of 1.0 molar amount of $SnCl_4$ to the mixture also resulted in larger downfield shift of these signals ($\delta = 3.12$ ppm ($\Delta\delta = +0.29$ ppm) and



SCHEME 1 Reaction of bis(*N*,*N*-dimethylcarbamoyl seleno)methane **1a** (R = C_6H_5) or **1e** (R = H) with $SnCl_4$ at a higher temperature.

$\delta = 3.44$ ppm ($\Delta\delta = +0.48$ ppm) assigned to the *N*,*N*-dimethylcarbamoyl group, and $\delta = 7.00$ ppm (broadening, $\Delta\delta = +0.89$ ppm) assigned to the methine proton) with retaining the symmetrical spectral pattern of **1a**. These results excluded out the formation of a tight **1a**-$SnCl_4$ complex in the reaction mixture, and a weak coordinating interaction between **1a** and $SnCl_4$ involving an association–dissociation equilibration was suggested [31]. Further standing of the mixture at 25°C for 24 h resulted in formation of β-1,3,5-triselenane **6a** ($\delta = 5.59$ ppm) as the main component besides diselenide **4** ($\delta = 3.06$ and 3.17 ppm) and a trace amount of benzaldehyde **7a** along with the formation of $CDCl_3$-insoluble products. The results of ^{1}H NMR monitoring of the reaction of **1a** with $SnCl_4$ (1.5 mol amt.) at 25°C are shown in Fig. 1.

On the other hand, little information was obtained from the ^{13}C NMR or ^{77}Se NMR monitoring of the reaction due to the broadening and complication of the signals. It is noteworthy that no signal assigned to the intermediates, such as acylselonium ion **A** or selenobenzaldehyde **3a**, was observed at all throughout the NMR monitoring experiments.

Generation and Trapping of Intermediary Selenoaldehydes **3** *and Acylselonium Ions* **A** *by using 2,3-Dimethyl-1,3-butadiene or Allyltrimethylsilane*

Selenoaldehydes are well recognized to behave as 2π dienophilies in Diels–Alder reactions with 1,3-butadienes to afford the corresponding [4 + 2]

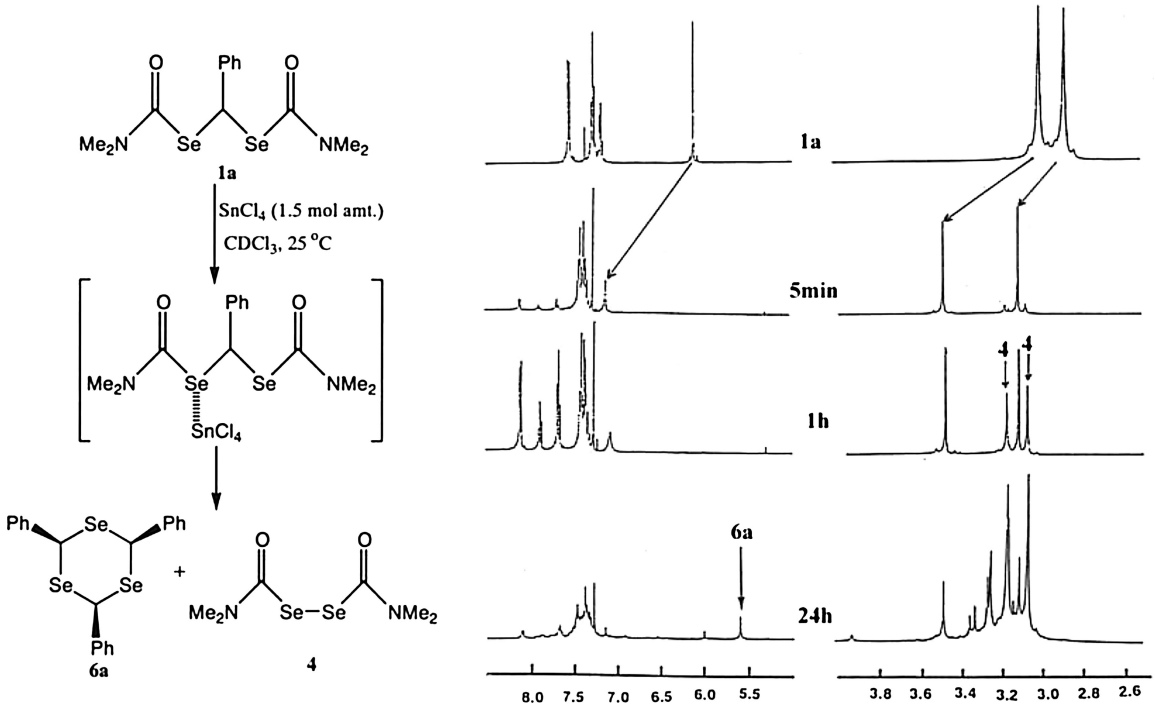
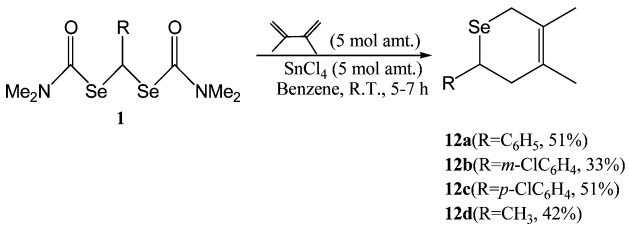


FIGURE 1 ^{1}H NMR monitoring experiment of the reaction of bis(*N*,*N*-dimethylcarbamoylseleno)methane **1a** (R = C_6H_5) with $SnCl_4$.

cycloadducts, and these reactions are generally applied to the successful trapping of in situ generated selenoaldehydes. Actually, when a benzene solution of **1a–d** was treated with $SnCl_4$ at RT in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene, the corresponding [4 + 2] cycloadducts **12a–c** were obtained in moderate yields (i.e., **12a**: 51%, **12b**: 33%, **12c**: 51%). The reaction of **1d** with $SnCl_4$ in the presence of 2,3-dimethyl-1,3-butadiene also formed relatively unstable cycloadduct **12d** in approximately 42% yield along with the contamination of a small amount of inseparable impurity. All the results are shown in Scheme 2. In contrast to the cases starting from **1a–d**, treatment of **1e** and **1f** with $SnCl_4$ under a similar reaction condition only gave the recovery of substrates, as was expected from the results of the reactions carried out in the absence of trapping agents.

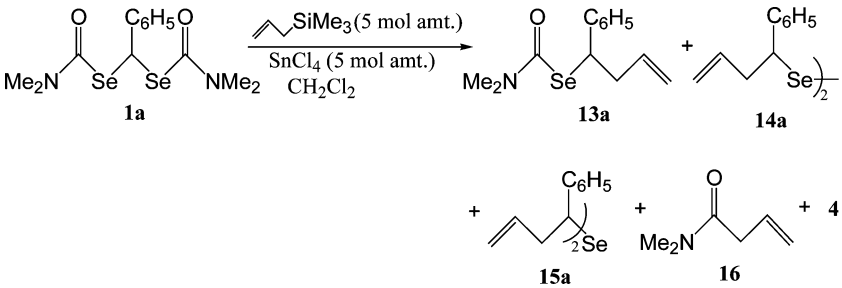
Furthermore, when a dichloromethane solution of **1a** was treated with $SnCl_4$ in the presence of allyltrimethylsilane at −70°C, selenocarbamate **13a**, allylation product of acylselonium ion **A**, was obtained in 60% yield besides diselenide **4** (5%) and the recovery of **1a** (15%). The yield of **13a** was lowered to 10% through the similar reaction carried out at 0°C, and an inseparable mixture of diselenide **14a** and monoselenide **15a** (**14a:15a** = 10:1, approximately), *N*,*N*-dimethyl-3-butenamide (**16** [48], 40%), allylation product of *N*,*N*-dimethylcarbamoyl cation (**C**), and **4** (11%) were obtained besides the recovery of **1a** (11%). All the results of the trapping experiments using allyltrimethylsilane are given in Table 3.



SCHEME 2 Trapping of selenoaldehydes **3** using 2,3-dimethyl-1,3-butadiene.

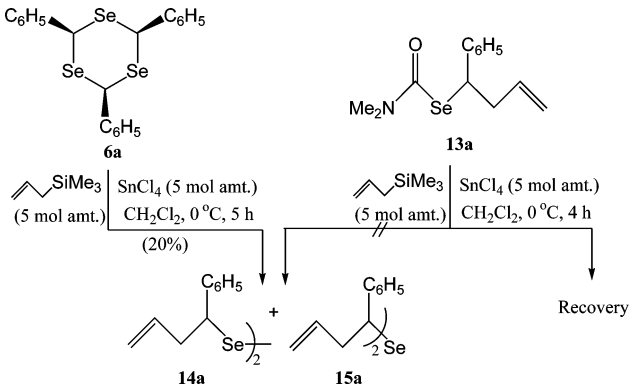
We already reported a one-step conversion of alkyl or alkenyl *N*,*N*-dimethylselenocarbamates or *N*,*N*-dimethyltellurocarbamates into the corresponding symmetrical dialkyl or dialkenyl dichalcogenides by treating with $SnCl_4$ [31]. However, it is noteworthy that the independent reaction of selenocarbamate **13a** with $SnCl_4$ in the presence of allyltrimethylsilane at 0°C only gave the recovery of **13a** besides a trace amount of complex mixture, and the treatment of β-1,3,5-triselenane **6a** with $SnCl_4$ in the presence of allyltrimethylsilane under a similar condition just gave a mixture of **14a** and **15a** in approximately 20% yield with a similar **14a:15a** ratio to that obtained through the reaction of **1** with $SnCl_4$ as shown in Scheme 3. Both **13a** and **16** were regarded as the allylation products of acylselonium ion **A** [49–58], generated through $SnCl_4$-induced removal of *N*,*N*-dimethylselenocarbamate ion from **1** and *N*,*N*-dimethylcarbamoyl cation (**C**), respectively, and the formation of **14a** and **15a** could also be explained by Lewis acid induced allylation of selenoaldehydes **3** generated through $SnCl_4$-catalyzed retro-[2 + 2 + 2]-type fragmentation of β-1,3,5-triselenanes **6** [6].

TABLE 3 Reaction of Bis(*N*,*N*-dimethylcarbamoylseleno)phenylmethane **1a** with $SnCl_4$ in the Presence of Allyltrimethylsilane



		Yield (%)					
Temperature (°C)	*Time (h)*	**13a**	**14a**	**15a**	**16**	**4**	Recovery
−70	2.5	60	0	0	0	5	15
0	5	10	20[a]	2[a]	40	11	11

[a]Yields of diselenide**14a** and monoselenide **15a** were estimated approximately from the integration of the ^{1}H NMR spectrum of the mixture.



SCHEME 3 Reactions of β-1,3,5-triselenane **6a** or *N,N*-dimethylselenocarbamate **13a** with $SnCl_4$ in the presence of allyltrimethylsilane.

Plausible Stepwise Pathway of $SnCl_4$-Induced Unsymmetrical Cleavage of Bis(N,N-dimethylcarbamoylseleno)methanes **1**

These results mentioned above just supported the stepwise pathway of conversion of **1** into **3** involving the formation of **A** at low temperature and the subsequent removal of *N,N*-dimethylcarbamoyl cation (**C**) from **A** at higher temperature as shown in Scheme 4. The formation of **4** could also be explained by aerobic oxidation of *N,N*-dimethylselenocarbamate ion–$SnCl_4$ complex **B** during standing and the usual workup procedure. All results just presented us a stepwise pathway of $SnCl_4$-induced conversion of **1** into selenoaldehydes **3** involving the formation of novel acylselonium ions **A** through weak coordinating interaction of $SnCl_4$ with **1** and the subsequent removal of *N,N*-dimethylcarbamoyl cation (**C**) from **A** at higher temperature as shown in Scheme 4. β-1,3,5-Triselenanes **6** were assumed to be afforded through elimination of stable *N,N*-dimethylcarbamoyl cation (**C**) from **A** and the subsequent trimerization of the resulting selenoaldehydes **3** in the final stage [4].

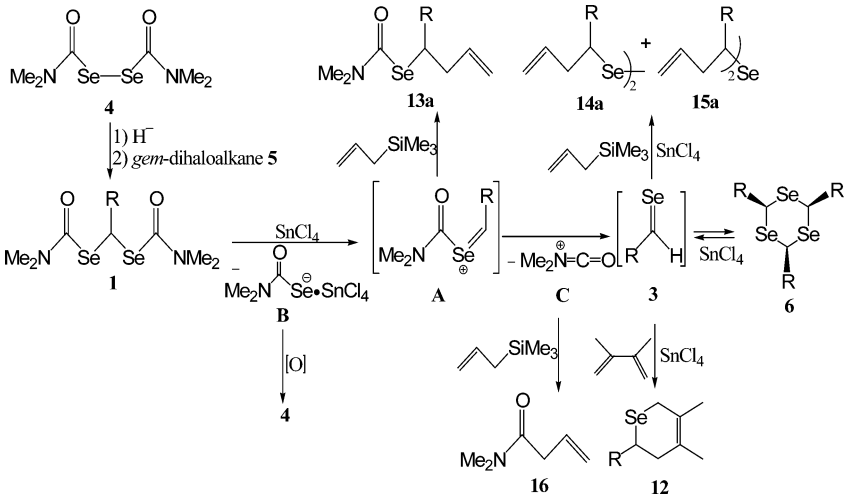
CONCLUSION

In conclusion, we found a new method for the generation of selenoaldehydes **3** through the reaction of bis(*N,N*-dimethylcarbamoylseleno)methanes **1** with $SnCl_4$ as well as the evidences of stepwise fragmentation pathway from **1** to **3** involving the formation of acylselonium ions **A**. Further attempts directed toward the generation of telluroaldehydes through a similar route starting from bis(*N,N*-dimethylcarbamoyl) ditelluride are under way in our laboratory.

EXPERIMENTAL

Instruments

The melting points were measured in open capillary tubes with a Buchi 535 micro-melting-point apparatus and were uncorrected. ^{1}H NMR spectra were recorded on a Bruker AC-400P spectrometer (400 MHz), and the chemical shifts of the ^{1}H NMR spectra are given in δ relative to internal tetramethylsilane (TMS). ^{13}C NMR spectra were recorded on a Bruker AC-400P spectrometer (100 MHz). ^{77}Se NMR spectra were recorded on a Bruker AC-400P spectrometer (76 MHz). Mass spectra were recorded on



SCHEME 4 Plausible stepwise pathway for the generation of selenoaldehydes **3** through the reaction of bis(*N,N*-dimethylcarbamoylseleno)methanes **1** with $SnCl_4$.

a Hitachi M-2000 mass spectrometer with electron-impact ionization at 20 or 70 eV using a direct inlet system. IR spectra were recorded for thin film (neat) or KBr disks on a JASCO FT/IR-7300 spectrometer. Elemental analyses were performed using a Yanagimoto CHN corder MT-5.

Materials

Column chromatography was performed using silica gel (Merck, Cat. No. 7734 or 9385) without a pretreatment. Dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$) were dried over P_4O_{10}, and were freshly distilled before use. Hexane, benzene, and *N,N*-dimethylformamide (DMF) were dried over calcium hydride (CaH_2) and freshly distilled before use. Ethanol was dried over anhydrous magnesium sulfate ($MgSO_4$), and was freshly distilled before use. All the substrates and reagents, including elemental selenium, benzal bromide, *m*-chlorobenzal bromide, *p*-chlorobenzal bromide, 1,1-dibromoethane, dibromomethane, ethyl dichloroacetate, 2,3-dimethyl-1,3-butadiene, allyltrimethylsilane, boron trifluoride diethyl ether complex ($BF_3{\cdot}OEt_2$), stannic chloride ($SnCl_4$), titanium tetrachloride ($TiCl_4$), *p*-toluenesulfonic acid, sodium metal, diisobutylaluminum hydride (DIBAH), sodium borohydride ($NaBH_4$), anhydrous sodium sulfate powder (Na_2SO_4), and molecular sieves 4A (MS-4A) were commercially available reagent grade, and were used without any pretreatment.

Synthesis of Bis(N,N-dimethylcarbamoylseleno)-methanes **1**

A 20 mL DMF solution of bis(*N,N*-dimethylcarbamoyl) diselenide (**4**, 906 mg, 3.00 mmol) was treated with sodium hydride (158 mg, 6.60 mmol) at 0°C to RT for 2 h and then with a *gem*-dihaloalkane **5** (4.50 mmol) at RT for 6 h. The reaction was quenched with an excess amount of water, and the reaction mixture was extracted with benzene. The organic layer was washed with brine, and was dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the residual crude mixture was subjected to column chromatographic separation on silica gel to afford bis(*N,N*-dimethylcarbamoylseleno)methanes **1**.

1a *($R = C_6H_5$).* Pale yellow needles, mp 184.2–185.6°C (dec.); MS (*m/z*): 394 (M^+; 3%, ^{80}Se), 250 ($C_6H_5CHSe_2$; 6%, ^{80}Se), 242 ($M^+ - C_3H_6NOSe$; bp, ^{80}Se), 170 (C_6H_5CHSe; 35%, ^{80}Se); IR (KBr): 2925, 1659, 1357, 1251, 1089, 890, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.87 (6H, br s), 2.99 (6H, br s), 6.12 (1H, s), 7.16–7.19 (1H, m), 7.25–7.29 (2H, m), 7.53–7.55 (2H, m); ^{13}C NMR ($CDCl_3$) δ: 36.6 (q), 36.9 (q), 40.4 (d), 127.26 (d), 127.29 (d), 128.2 (d), 143.1 (s), 164.6 (s). Calcd for $C_{13}H_{18}N_2O_2Se_2$: C, 39.81; H, 4.62; N, 7.14%. Found: C, 39.29; H, 4.59; N, 6.80%.

1b *($R = m\text{-}ClC_6H_4$).* Pale yellow needles, mp 93.9–95.4°C; MS (*m/z*): 428 (M^+; 1%, ^{80}Se, ^{35}Cl), 72 ($CONMe_2$; bp); IR (KBr): 2928, 1679, 1569, 1477, 1361, 1249, 1092, 888, 669 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.87 (6H, s), 3.00 (6H, s), 6.05 (1H, s), 7.15–7.54 (4H, m); ^{13}C NMR ($CDCl_3$) δ: 36.7 (q), 36.8 (q), 39.2 (d), 126.4 (d), 127.3 (d), 128.3 (d), 129.4 (d), 133.8 (s), 145.1 (s), 164.2 (s). Calcd for $C_{13}H_{17}ClN_2O_2Se_2$: C, 36.60; H, 4.02; N, 6.57%. Found: C, 37.27; H, 4.12; N, 6.46%.

1c *($R = p\text{-}ClC_6H_4$).* Colorless needles, mp 115.8–117.7°C; MS (*m/z*): 428 (M^+; 10%, ^{80}Se, ^{35}Cl), 276 ($M^+ -$ $SeCONMe_2$; 49%, ^{80}Se, ^{35}Cl), 224 ($M^+ - p$-ClC_6H_4CHSe; 5%, ^{80}Se, ^{35}Cl), 72 ($CONMe_2$; bp); IR (KBr): 2922, 2852, 1664, 1588, 1508, 1485, 1362, 1256, 1097, 835 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.87 (6H, s), 3.00 (6H, s), 6.05 (1H, s), 7.22–7.27 (2H, m), 7.47–7.50 (2H, m); ^{13}C NMR ($CDCl_3$) δ: 36.7 (q), 36.9 (q), 39.2 (d), 128.3 (d), 129.6 (d), 132.8 (s), 141.8 (s), 164.4 (s). Calcd for $C_{13}H_{17}ClN_2O_2Se_2$: C, 36.60; H, 4.02; N, 6.57%. Found: C, 36.43; H, 4.08; N, 6.52%.

1d *($R = CH_3$).* Yellow oil; MS (*m/z*): 332 (M^+; 1%, ^{80}Se), 260 ($M^+ - CONMe_2$; 3%, ^{80}Se), 224 ($M^+ - CH_3CHSe$; 5%, ^{80}Se), 72 ($CONMe_2$; bp); IR (neat): 2920, 1661, 1480, 1439, 1362, 1257, 1090, 895 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.08 (3H, d, $J = 7.2$ Hz), 2.91 (6H, s), 3.03 (6H, s), 5.05 (1H, q, $J = 7.2$ Hz); ^{13}C NMR ($CDCl_3$) δ: 26.6 (q), 33.6 (s), 36.4 (q), 36.9 (q), 165.2 (s). Calcd for $C_8H_{16}N_2O_2Se_2$: C, 29.10; H, 4.88; N, 8.49%. Found: C, 29.38; H, 4.59; N, 8.20%.

1e *($R = H$).* Colorless needles, mp 102.7–103.3°C (dec.); MS (*m/z*): 318 (M^+; 5%, ^{80}Se), 72 ($CONMe_2$; bp); IR (KBr): 2921, 1656, 1363, 1258, 1098, 896, 653 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.92 (6H, br s), 3.04 (6H, br s), 4.32 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 18.1 (t), 36.7 (q), 37.1 (q), 165.2 (s). Calcd for $C_7H_{14}N_2O_2Se_2$: C, 26.59; H, 4.46; N, 8.86%. Found: C, 26.66; H, 4.60; N, 8.57%.

1f *($R = CO_2C_2H_5$).* Yellow oil; MS (*m/z*): 390 (M^+; 15%, ^{80}Se), 222 ($M^+ - CHSeCO_2C_2H_5$; 82%, ^{80}Se), 72 ($CONMe_2$; bp); IR (neat): 2980, 1728, 1661, 1365, 1273, 1258, 1096, 890, 673 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.23 (3H, t, $J = 7.0$ Hz), 2.88 (6H, br s), 2.99 (6H, br s), 4.78 (2H, q, $J = 7.0$ Hz), 5.52 (1H, s); ^{13}C NMR ($CDCl_3$) δ: 13.9 (q), 36.4 (d), 36.8 (q), 36.9 (q),

62.4 (t), 163.7 (s), 170.2 (s). Calcd for $C_{10}H_{18}N_2O_4Se_2$: C, 30.93; H, 4.64; N, 7.22%. Found: C, 31.08; H, 4.51; N, 7.06%.

Reaction of Bis(N,N-dimethylcarbamoylseleno)-methanes **1** *with* $SnCl_4$

A dry dichloromethane or benzene solution of **1** (1.00 mmol) was treated with $SnCl_4$ (1.305 g, 5.00 mmol) at RT under an Ar atmosphere for a few hours. The reaction was quenched with an excess amount of aqueous $NaHCO_3$ solution, and the reaction mixture was extracted with chloroform. The organic layer was washed with water, and was dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the residual crude mixture was subjected to chromatographic separation on silica gel to afford β-1,3,5-triselenanes **6**.

6a *($R = C_6H_5$).* (Known compound); colorless needles, mp 197.7–198.5°C (lit. [6, 35], 195.0–208.0°C); MS (*m/z*): 170 (M^+/3; bp, ^{80}Se); IR (KBr): 2927, 1491, 1475, 1450, 777, 697, 479 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 5.59 (3H, s), 7.27–7.36 (15H, m); ^{13}C NMR ($CDCl_3$) δ: 45.8 (d), 127.8 (d), 128.5 (d), 129.1 (d), 139.2 (s). Calcd for $C_{21}H_{18}Se_3$: C, 49.72; H, 3.58%. Found: C, 49.57; H, 3.54%.

6b *($R = m\text{-}ClC_6H_4$).* Colorless needles, mp 180.7–183.3°C; MS (*m/z*): 204 (M^+/3; bp, ^{80}Se, ^{35}Cl), 169 (*m*-ClC_6H_4CSeH–Cl; 31%, ^{80}Se, ^{35}Cl), 155 (bp); IR (KBr): 3067, 1590, 1471, 1422, 1130, 1076, 874, 790, 711 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 5.50 (3H, s), 7.25–7.45 (12H, m); ^{13}C NMR ($CDCl_3$) δ: 44.8 (d), 125.9 (d), 127.9 (d), 128.9 (d), 130.5 (d), 134.9 (s), 140.5 (s). Calcd for $C_{21}H_{15}Cl_3Se_3$: C, 41.31; H, 2.48%. Found: C, 41.47; H, 2.45%.

6c *($R = p\text{-}ClC_6H_4$).* (Known compound); colorless needles, mp 183.1–186.1°C (lit. [10], 184.0–185.0°C); MS (*m/z*): 276 (bp), 274 (5%), 224 (42%), 206 (M^+/3; 3%, ^{80}Se, ^{37}Cl), 204 (M^+/3; 18%, ^{80}Se, ^{35}Cl), 203 (M^+/3-1; 27%, ^{80}Se, ^{35}Cl); IR (KBr): 2930, 1487, 1404, 1102, 1011, 835, 756, 729, 647 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 5.51 (3H, s), 7.32–7.38 (12H, m); ^{13}C NMR ($CDCl_3$) δ: 44.8 (d), 129.1 (d), 129.5 (d), 134.5 (s), 137.2 (s). Calcd for $C_{21}H_{15}Cl_3Se_3 \cdot CHCl_3$: C, 36.13; H, 2.20%. Found: C, 36.48; H, 2.37%.

6d *($R = CH_3$).* (Known compound); yellow needles, mp 139.1–140.3°C (lit. [34], 144°C); MS (*m/z*): 324 (M^+; 21%, ^{80}Se), 108 (M^+/3; 94%, ^{80}Se), 55 (bp); IR (KBr): 2948, 1436, 1370, 1153, 1027, 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.82 (9H, d, $J = 7.0$ Hz), 4.35 (3H, q, $J = 7.0$ Hz); ^{13}C NMR ($CDCl_3$) δ: 21.8 (q), 34.1 (d). Calcd for $C_6H_{12}Se_3$: C, 22.45; H, 3.77%. Found: C, 22.51, H, 3.76%.

Reaction of Bis(N,N-dimethylcarbamoylseleno)-phenylmethane **1a** *with* $SnCl_4$ *under an Aerobic Condition*

A dichloromethane solution of **1a** (392 mg, 1.00 mmol) was treated with $SnCl_4$ (1.305 g, 5.00 mmol) at RT under an aerobic condition for 4 h. The reaction was quenched with an excess amount of aqueous $NaHCO_3$solution, and the reaction mixture was extracted with chloroform. The organic layer was washed with water, and was dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the residual crude mixture was subjected to chromatographic separation on silica gel to obtain benzaldehyde **7a** and **4**.

Reaction of Bis(N,N-dimethylcarbamoylseleno)-methane **1a** *with* $SnCl_4$ *at a Higher Temperature*

A 10 mL chloroform solution **1a** (392 mg, 1.00 mmol) was treated with $SnCl_4$ (783 mg, 3.00 mmol) at refluxing temperature for 16 h in the presence of MS-4A. The reaction was quenched with an excess amount of aqueous $NaHCO_3$ solution, and the mixture was extracted with chloroform. The organic layer was washed with water, and was dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the crude mixture was subjected to column chromatographic separation on silica gel to afford a *cis–trans* mixture of 1,2,4-triselenolane **8a** (about 1:1, estimated by the integration of ^1H NMR spectra of the mixture), selenocarbamate **9a**, and diselenide **4**. The mixture of **8a** was subjected to repeated column chromatography on silica gel to obtain a small amount of one isomer of **8a** (isomer 1).

8a *($R = C_6H_5$, Isomer-1).* Orange crystals, mp 99.4–100.6°C (dec.); MS (*m/z*): 420 (M^+; 2%, ^{80}Se), 250 ($PhCHSe_2$; 2%, ^{80}Se), 170 (PhCHSe; bp, ^{80}Se); IR (KBr): 3025, 2925, 1491, 1449, 775, 695, 668, 632 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 6.91 (2H, s), 7.21–7.36 (6H, m), 7.65–7.68 (4H, m); ^{13}C NMR ($CDCl_3$) δ: 55.8 (d), 127.7 (d), 128.5 (d), 128.8 (d), 139.0 (s); ^{77}Se NMR ($CDCl_3$) δ: 660.7, 701.0.

8a *($R = C_6H_5$, Isomer-2).* Orange crystals, mp 102.5–104.0°C (dec.); MS (*m/z*): 420 (M^+; 3%, ^{80}Se), 250 ($PhCHSe_2$; 5%, ^{80}Se), 170 (PhCHSe; bp, ^{80}Se); IR (KBr): 3025, 2936, 1490, 776, 771, 694, 643 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 6.48 (2H, s), 7.32–7.36 (6H, m), 7.74–7.77 (4H, m).

9a *($R = C_6H_5$).* Yellow oil; MS (*m/z*): 413 (M^+; 2%, ^{80}Se), 322 ($M^+ - CH_2Ph$; 10%, ^{80}Se), 261 ($M^+ - SeCONMe_2$; bp, ^{80}Se); IR (neat): 3026, 2928, 1668, 1493, 1361, 1094, 893, 760, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.88 (3H, s), 2.98 (3H, s), 3.85 (2H, dd, $J = 5.1$ Hz), 5.66 (1H, s), 7.17–7.44 (10H, m); ^{13}C NMR ($CDCl_3$) δ: 31.9 (t), 36.7 (q), 36.9 (q), 39.1 (d), 126.8 (d), 127.5 (d), 128.0 (d), 128.5 (d), 128.6 (d), 129.0 (d), 138.2 (s), 142.2 (s), 164.9 (s). Calcd for $C_{17}H_{19}NOSe_2$: C, 49.65; H, 4.66; N, 3.41%. Found: C, 49.73; H, 4.63; N, 3.15%.

Reaction of Bis(N,N-dimethylcarbamoylseleno)-methane **1e** *with $SnCl_4$ at a Higher Temperature*

A 10 mL chloroform solution **1e** (316 mg, 1.00 mmol) was treated with $SnCl_4$ (783 mg, 3.00 mmol) at refluxing temperature for 16 h in the presence of MS-4A. The reaction was quenched with an excess amount of aqueous $NaHCO_3$ solution, and the mixture was extracted with chloroform. The organic layer was washed with water, and was dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the crude mixture was subjected to column chromatographic separation on silica gel to afford insoluble compound **10e**, characterized to polymethylene selenide, and 1,2,4,5-tetraselenane **11e**, along with diselenide **4** and trace amounts of uncharacterized products.

10e *($R = H$).* Colorless solid, mp 170.3–172.1°C (lit. [47], 165°C); IR (KBr): 3040, 1605, 1402, 1383, 1231, 1118, 700, 466 cm^{-1}.

11e *($R = H$).* Yellow crystals, mp 94°C; MS (*m/z*): 348 (M^+; 78%, ^{80}Se), 174 (CH_2Se_2; 54%, ^{80}Se), 94 (CH_2Se; 63%, ^{80}Se); IR (KBr): 2915, 1347, 1117, 1089, 761, 739 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 4.62 (4H, s). Calcd for $C_2H_4Se_4$: C, 6.99; H, 1.17%. Found: C, 7.36; H, 1.31%.

Reaction of Bis(N,N-dimethylcarbamoylseleno)-methanes **1** *with $SnCl_4$ in the Presence of 2,3-Dimethyl-1,3-butadiene*

2,3-Dimethyl-1,3-butadiene (411 mg, 5.00 mmol) was added to a dry benzene solution of **1** (1.00 mmol), and then the reaction mixture was treated with $SnCl_4$ (1.305 g, 5.00 mmol) at RT for a few hours under an Ar atmosphere. The reaction was quenched with an excess amount of aqueous $NaHCO_3$ solution, and the reaction mixture was extracted with chloroform. The organic layer was washed with water, and was dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the residual crude mixture was subjected to column chromatographic separation on silica gel to afford the corresponding [4 + 2] cycloadducts **12**.

12a *($R = C_6H_5$).* (Known compound) [12, 15].

12b *($R = m\text{-}ClC_6H_4$).* Pale yellow oil; MS (*m/z*): 286 (M^+; 55%, ^{80}Se, ^{35}Cl), 206 ($M^+ - Se$; 45%, ^{80}Se, ^{35}Cl), 204 ($M^+ - H_2Se$; bp, ^{35}Cl); IR (neat): 2919, 1598, 1569, 1474, 1428, 1381, 1079, 882, 785, 739, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.74 (3H, s), 1.83 (3H, s), 2.51 (1H, dd, $J = 16.7$, 2.6 Hz), 2.67 (1H, dd, $J = 16.4$, 10.0 Hz), 3.11 (1H, d, $J = 14.9$ Hz), 3.39 (1H, d, $J = 14.9$ Hz), 4.15 (1H, dd, $J = 10.1$, 4.1 Hz), 7.17–7.33 (4H, m); ^{13}C NMR ($CDCl_3$) δ: 19.8 (q), 20.7 (q), 24.1 (dd), 38.0 (d), 40.5 (dd), 125.0 (s), 125.7 (d), 127.0 (d), 127.6 (d), 129.7 (s), 134.2 (s), 145.7 (s). Calcd for $C_{13}H_{15}ClSe$: C, 54.66; H, 5.29%. Found: C, 55.04; H, 5.21%.

12c *($R = p\text{-}ClC_6H_4$).* (Known compound) [12]; pale yellow oil; MS (*m/z*): 286 (M^+; bp, ^{80}Se, ^{35}Cl); IR (neat): 2988, 2915, 1490, 1407, 1089, 1014, 829, 738 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.74 (3H, s), 1.83 (3H, s), 2.50 (1H, dd, $J = 16.7$, 3.2 Hz), 2.66 (1H, dd, $J = 16.7$, 10.0 Hz), 3.10 (1H, d, $J = 14.9$ Hz), 3.39 (1H, d, $J = 14.9$ Hz), 4.17 (1H, dd, $J = 10.0$, 4.1 Hz), 7.20–7.32 (4H, m); ^{13}C NMR ($CDCl_3$) δ: 19.8 (q), 20.8 (q), 24.0 (dd), 37.7 (d), 40.6 (dd), 125.0 (s), 128.3 (d), 128.6 (d), 129.1 (s), 132.4 (s), 142.2 (s). Calcd for $C_{13}H_{15}ClSe$: C, 54.66; H, 5.29%. Found: C, 54.42; H, 5.20%.

12d *($R = CH_3$).* Pale yellow oil; MS (*m/z*): 190 (M^+; 47%, ^{80}Se), 109 ($M^+ - Se$-1; 7%), 67 (C_5H_7; bp); IR (neat): 2957, 2868, 1668, 1455, 1375, 1216, 759 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.39 (3H, d, $J = 6.8$ Hz), 1.72 (3H, s), 1.78 (3H, s), 2.18 (1H, dd, $J = 15.6$, 9.9 Hz), 2.31 (1H, dd, $J = 15.6$, 2.6 Hz), 2.98 (1H, d, $J = 14.8$ Hz), 3.19 (1H, dd, $J = 9.6$, 4.1 Hz), 3.25 (1H, d, $J = 14.7$ Hz).

Reaction of Bis(N,N-dimethylcarbamoylseleno)-methane **1a** *with $SnCl_4$ in the Presence of Allyltrimethylsilane*

Allyltrimethylsilane (571 mg, 5.00 mmol) was added to a dry dichloromethane solution of **1a** (392 mg, 1.00 mmol), then the reaction mixture was treated with $SnCl_4$ (1.305 g, 5.00 mmol) at 0°C or −70°C for a few hours under an Ar atmosphere. The reaction was quenched with an excess amount of aqueous $NaHCO_3$ solution, and the reaction mixture was extracted with chloroform. The organic layer was washed with water and was dried over anhydrous

Na_2SO_4 powder. After removing the solvent in vacuo, the residual crude mixture was subjected to chromatographic purification using silica gel to separate products **13a,16**, and the inseparable mixture of **14a** and **15a**.

13a *($R = C_6H_5$).* Pale yellow oil; MS (*m/z*): 283 (M^+; 2%, ^{80}Se), 153 ($SeCONMe_2$; 23%, ^{80}Se), 131 ($M^+ - SeCONMe_2$; bp), 72 ($CONMe_2$; 98%); IR (neat): 2924, 1731, 1667, 1454, 1361, 1260, 896, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.80 (3H, s), 2.84–2.90 (2H, m), 2.93 (3H, s), 4.64 (1H, t, $J = 8.6$ Hz), 4.96 (1H, br d, $J = 10.0$ Hz), 5.04 (1H, br d, $J = 17.0$ Hz), 5.70 (1H, ddt, $J = 17.0$, 10.0, 6.9 Hz), 7.14–7.33 (5H, m); ^{13}C NMR ($CDCl_3$) δ: 36.3 (q), 36.9 (q), 40.9 (t), 47.0 (d), 116.8 (br s), 126.8 (d), 127.7 (br s), 128.3 (d), 135.7 (d), 142.2 (s), 164.9 (s). Calcd for $C_{13}H_{17}NSe$: C, 55.32; H, 6.07; N, 4.96%. Found: C, 55.67; H, 6.12; N, 4.83%.

14a + 15a *($R = C_6H_5$,* **14a:15a** *= 10:1, Estimated Approximately from the Integration of the ^1H NMR Spectrum of the Mixture).* Yellow oil; MS (*m/z*): 422 (M^+ (**14a**); 2%, ^{80}Se), 342 (M^+ (**15a**); 1%, ^{80}Se), 262 (M^+ (**14a**)-Se_2 and/or M^+ (**15a**)-Se; bp); IR (neat): 2927, 2350, 1732, 1642, 1495, 1454, 1250, 1106, 1029, 840, 759, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.20–2.90 (4H, m), 4.80–5.30 (4H, m), 5.60–5.90 (2H, m), 7.20–7.50 (10H, m).

16. (Known compound) [48]

Reaction of Allylation Product **13a** *with $SnCl_4$*

A dry dichloromethane solution of allylation product **13a** (282 mg, 1.00 mmol) and allyltrimethylsilane (571 mg, 5.00 mmol) was treated with $SnCl_4$ (1.305 g, 5.00 mmol) at 0°C for 4 h. The reaction was quenched with an excess amount of aqueous $NaHCO_3$ solution, and the mixture was extracted with chloroform. The organic layer was washed with water, and was dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the crude mixture was subjected to column chromatographic separation on silica gel to afford the recovery of **13a** in almost quantitative yield along with the formation of a trace amount of complex mixture.

Reaction of β-1,3,5-Triselenane **6a** *with $SnCl_4$ in the Presence of Allyltrimethylsilane*

A dry dichloromethane solution of β-1,3,5-tiselenane **6a** ($R = C_6H_5$, 507 mg, 1.00 mmol) was treated with $SnCl_4$ (1.305 g, 5.00 mmol) in the presence of allyltrimethylsilane (571 mg, 5.00 mmol) at 0°C for 5 h. The reaction was quenched with an excess amount of aqueous $NaHCO_3$ solution, and the mixture was extracted with chloroform. The organic layer was washed with water, and was dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the crude mixture was subjected to column chromatographic separation on silica gel to afford the inseparable mixture of diselenide **14a** and monoselenide **15a** as the main components.

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