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Novel generation of selenoaldehydes through stannic chloride-induced unsymmetrical C–Se bond cleavage of bis(*N*,*N*-dimethylcarbamoylseleno)methanes

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Abstract—Treatment of a benzene or a CH_2Cl_2 solution of bis(*N*,*N*-dimethylcarbamoylseleno)methanes with $SnCl_4$ afforded β-1,3,5-triselenanes, and the key intermediates, 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.

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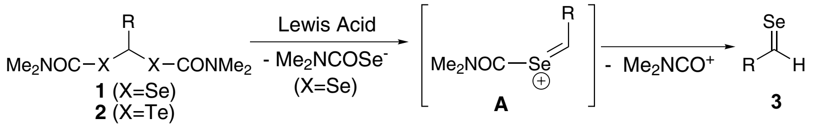
Recently, various methodologies for the generation of selenoaldehydes **3** have been reported in the light of their structural interests and the potentiality as new reactive intermediates for the organic reactions.[1] However, few studies on the conversion of symmetrical diseleno- or ditelluroacetals into the corresponding chalcogenoaldehydes or chalcogenoketones were achieved due to the liability of the target species and the lack of preparative methods of suitable dichalcogenoacetals as the precursors of chalcogenoaldehydes. In the course of our studies on the novel generation of highly-reactive species related to higher-raw chalcogenocarbonyl compounds, we previously found a convenient preparation of stable ditelluroacetal derivatives **2** through the reaction of *N*,*N*-dimethyltellurocarbamate ions with *gem*-dihaloalkanes.[1r,2] These results urged us to the preparation and the further reaction of symmetrical diselenoacetals **1** with a Lewis acid on the basis of the coordinating interaction between the selenocarbamate moiety and a soft Lewis acid.[3] Actually, diselenoacetals **1** are expected to undergo Lewis acid-induced unsymmetrical C–Se bond cleavage to generate selenoaldehydes **3** via acylselonium ions **A** through the push–pull type removal of *N*,*N*-dimethylselenocarbamate ion and *N*,*N*-dimethylcarbamoyl cation.[4] According to our expectation as mentioned above, we started our exploration on the reaction of **1** with a Lewis acid in the presence or absence of trapping agents. In this letter, we describe 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 pathway of **1** involving the in situ formation of key intermediates **A** as the precursors of **3**.

Bis(*N*,*N*-dimethylcarbamoyl)diselenide (**4**)[5] was prepared by treating DMF with sodium metal and elemental selenium at 100–110 °C followed by an aerobic exposure at rt. Subsequently, stepwise treatment of a DMF solution of diselenide **4** with NaH[6] and a *gem*-dihaloalkane (benzal bromide (**5a**), *m*-chlorobenzal bromide (**5b**), *p*-chlorobenzal bromide (**5c**), 1,1-dibromoethane (**5d**), dibromomethane (**5e**), and ethyl



Keywords: Bis(*N*,*N*-dimethylcarbamoylseleno)methane; Diselenoacetal; Selenoaldehyde; β-1,3,5-Triselenane; Acylselonium ion.

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dichloroacetate (**5f**), respectively) afforded highly air-stable bis(*N*,*N*-dimethylcarbamoylseleno)methanes **1** (i.e., **1a**: 60%, **1b**: 37%, **1c**: 21%, **1d**: 59%, **1e**: 31%, and **1f**: 46%, respectively),[2] which are regarded as symmetrical diselenoacetals bearing a removable *N*,*N*-dimethylcarbamoyl group on each selenium atom.

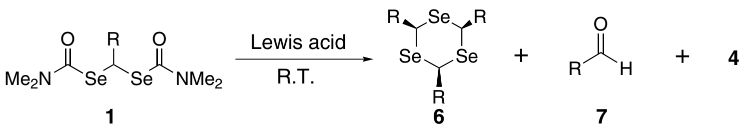
Treating a CH_2Cl_2, a $CHCl_3$, or a benzene solution of **1a–f** with TsOH or a hard Lewis acid, such as $BF_3 \cdot OEt_2$, resulted in the recovery of **1** in all cases. On the other hand, treatment of **1a–d** with $SnCl_4$ (2.0 mol amt.) at rt under an Ar atmosphere afforded β-1,3,5-triselenanes **6a–d**, the trimers of selenoaldehydes **3a–d**, along with the recovery of **1**. The yields of **6** were efficiently improved by the use of 3.0–5.0 mol amt. of $SnCl_4$, and in such cases neither the stereoisomers of **6a–d** nor any other byproducts, 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 reaction conditions. Interestingly, a similar treatment of **1a** with $SnCl_4$ under an aerobic atmosphere just gave benzaldehyde (**7a**) as main products besides **4**. All the results are given in Table 1.

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 spectra of the reaction mixture revealed a slight downfield shift with the complete retaining of their original symmetrical spectral pattern involving a singlet methine proton and a pair of sharp singlet signals assigned to the *N*,*N*-dimethylcarbamoyl groups. Further addition of $SnCl_4$ (1.5 mol amt.) to the mixture also resulted in larger downfield shift of these signals ($\delta = 3.12$ ppm ($\Delta\delta = +0.29$ ppm) and 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 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. Further standing of the mixture for 24 h at 25 °C resulted in the formation of β-1,3,5-triselenane **6a** ($\delta = 5.59$ ppm) as main component besides diselenide **4** ($\delta = 3.06$, 3.17 ppm) and a trace amount of benzaldehyde (**7a**) along with the formation of $CDCl_3$-insoluble products. 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 selenoaldehyde **3a**, was observed at all throughout the NMR monitoring experiments.

Trapping of selenoaldehydes **3** was efficiently carried out by treating a benzene solution of **1** with $SnCl_4$ in the presence of 2,3-dimethyl-1,3-butadiene (**8**) to afford the [4+2] cycloadducts **9** as shown in Scheme 1. Furthermore, when a CH_2Cl_2 solution of **1a** was treated with $SnCl_4$ in the presence of allyltrimethylsilane (**10**) at −70 °C, compound **11a** was obtained in 24% yield besides **4** (5%) and the recovery of **1a** (53%). The yield of **11a** was lowered to 10% by carrying out the same reaction at 0 °C, by which an inseparable mixture of diselenide **12a** and monoselenide **13a** (**12a**:**13a** = 10:1, approximately), *N*,*N*-dimethyl-3-butenamide (**14**,[8] 40%, allylation product of acyl cation **C**), and **4** (11%) were obtained besides the recovery of **1a** (11%). All the results of the trapping experiments using allyltrimethylsilane (**10**) are given in Table 2.

It is noteworthy that the independent reaction of selenocarbamate **11a** with $SnCl_4$ in the presence of allyltrimethylsilane (**10**) at 0 °C only gave the recovery of **11a**

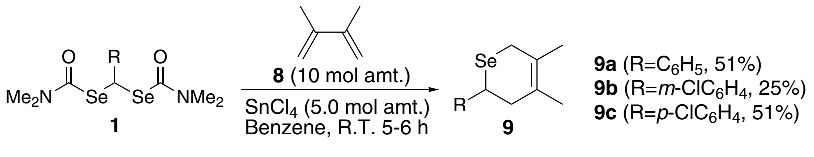
Table 1. $SnCl_4$-induced conversion of **1** into β-1,3,5-triselenanes **6**



Substrate/**1**, R	Lewis acid (mol amt.)	Solvent	Time/h	Yield/%			
				6	**7**	**4**	Recov.
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	56 (**6a**)[a]	Trace (**7a**)	Trace	16
m-ClC_6H_4 (**1b**)	$SnCl_4$ (5.0)	Benzene	1	41 (**6b**)	Trace (**7b**)	Trace	Trace
p-ClC_6H_4 (**1c**)	$SnCl_4$ (5.0)	Benzene	6	43 (**6c**)[a]	Trace (**7c**)	Trace	Trace
CH_3 (**1d**)	$SnCl_4$ (3.0)	CH_2Cl_2	24	15 (**6d**)[a]	0[b]	Trace	5

[a] Refs. 1k,p, and 7.

[b] Acetaldehyde (**7d**) was not found or detected at all in the crude mixture maybe due to evaporation during the workup procedure.



Scheme 1. Trapping of selenoaldehydes **3** using 2,3-dimethyl-1,3-butadiene (**8**).

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