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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<sub>4</sub> afforded  $\beta$ -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. © 2005 Elsevier Ltd. All rights reserved.

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.<sup>1</sup> 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.<sup>1r,2</sup> 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.<sup>3</sup> Actually, diselenoacetals 1 are expected to undergo Lewis acid-induced unsym-

metrical 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.<sup>4</sup> 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<sub>4</sub> 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)<sup>5</sup> 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<sup>6</sup> and a gemdihaloalkane (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;  $\beta$ -1,3,5-Triselenane; Acylselonium ion.

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

Treating a CH<sub>2</sub>Cl<sub>2</sub>, a CHCl<sub>3</sub>, or a benzene solution of **1a**–**f** with TsOH or a hard Lewis acid, such as BF<sub>3</sub>·OEt<sub>2</sub>, resulted in the recovery of 1 in all cases. On the other hand, treatment of **1a-d** with SnCl<sub>4</sub> (2.0 mol amt.) at rt under an Ar atmosphere afforded  $\beta$ -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<sub>4</sub>, 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<sub>4</sub> under the similar reaction conditions. Interestingly, a similar treatment of 1a with SnCl<sub>4</sub> under an aerobic atmosphere just gave benzaldehyde (7a) as main products besides 4. All the results are given in Table 1.

When a CDCl<sub>3</sub> solution of **1a** was treated with SnCl<sub>4</sub> (0.5 mol amt.) in an NMR tube at 25 °C, the signals of the <sup>1</sup>H 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<sub>4</sub> (1.5 mol amt.) to the mixture also resulted in larger downfield shift of these signals  $(\delta = 3.12 \text{ ppm} (\Delta \delta = +0.29 \text{ ppm}) \text{ and } 3.44 \text{ ppm} (\Delta \delta =$ +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 spec-

Table 1. SnCl<sub>4</sub>-induced conversion of 1 into  $\beta$ -1,3,5-triselenanes 6

tral pattern of 1a. These results excluded out the formation of a tight **1a**–SnCl<sub>4</sub> complex in the reaction mixture, and a weak coordinating interaction between 1a and SnCl<sub>4</sub> involving an association-dissociation equilibration was suggested. Further standing of the mixture for 24 h at 25 °C resulted in the formation of  $\beta$ -1,3,5triselenane **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<sub>3</sub>-insoluble products. On the other hand, little information was obtained from the <sup>13</sup>C NMR or <sup>77</sup>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<sub>4</sub> 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<sub>2</sub>Cl<sub>2</sub> solution of 1a was treated with SnCl<sub>4</sub> 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<sub>4</sub> in the presence of allyltrimethylsilane (10) at 0 °C only gave the recovery of 11a

$Me_2N \xrightarrow{H} Se^{Se} NMe_2 \xrightarrow{H} R.T. \xrightarrow{R} R \xrightarrow{H} H + 4$ $1 \qquad 6 \qquad 7$							
Substrate/1, R	Lewis acid (mol amt.)	Solvent	Time/h	Yield/%			
				6	7	4	Recov.
$C_{6}H_{5}(1a)$	BF <sub>3</sub> ·OEt <sub>2</sub> (2.0)	$CH_2Cl_2$	1	0	0	0	Quant.
$C_{6}H_{5}$ (1a)	SnCl <sub>4</sub> (3.0)	$CH_2Cl_2$	1	56 ( <b>6a</b> ) <sup>a</sup>	Trace (7a)	Trace	16
m-ClC <sub>6</sub> H <sub>4</sub> (1b)	$SnCl_4$ (5.0)	Benzene	1	41 ( <b>6b</b> )	Trace (7b)	Trace	Trace
p-ClC <sub>6</sub> H <sub>4</sub> (1c)	SnCl <sub>4</sub> (5.0)	Benzene	6	$43 (6c)^{a}$	Trace (7c)	Trace	Trace
CH <sub>3</sub> (1d)	SnCl <sub>4</sub> (3.0)	$CH_2Cl_2$	24	15 ( <b>6d</b> ) <sup>a</sup>	0 <sup>b</sup>	Trace	5

R\_Se\_R ö

<sup>a</sup> Refs. 1k,p, and 7.

<sup>b</sup> 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).

Table 2. Reaction of bis(N,N)-dimethylcarbamoylseleno)phenylmethane (1a) with  $SnCl_4$  in the presence of allyltrimethylsilane (10)



<sup>a</sup> Yields of diselenide **12a** and monoselenide **13a** were estimated approximately from the integration of the <sup>1</sup>H NMR spectrum of the mixture.



Scheme 2. Plausible stepwise pathway for the generation of selenoaldehydes 3 through the reaction of bis(N,N-dimethylcarbamoylseleno) methanes 1 with SnCl<sub>4</sub>.

and the treatment of 6a with SnCl<sub>4</sub> in the presence of 10under a similar condition just gave a mixture of 12a and 13a with a similar 12a:13a ratio to that obtained through the reaction of 1 with SnCl<sub>4</sub>. Both 11a and 14 were regarded as the allylation products of acylselonium ion A, generated through SnCl<sub>4</sub>-induced removal of N,N-dimethylselenocarbamate ion from 1, and N,Ndimethylcarbamoyl cation (C), respectively, and these results supported the stepwise pathway of conversion of 1 into selenoaldehydes 3 involving the formation of  $A^9$  at low temperature and the subsequent removal of N,N-dimethylcarbamoyl cation (C) from A at higher temperature as shown in Scheme 2. The formation of 4 could also be explained by aerobic oxidation of  $N_{N}$ dimethylselenocarbamate ion-SnCl<sub>4</sub> complex B during standing and the usual workup procedure.

In conclusion, we found a new method for the generation of selenoaldehydes **3** through the reaction of bis(N,N-dimethylcarbamoylseleno)methanes**1**withSnCl<sub>4</sub> as well as the evidences of stepwise fragmentationpathway from**1**to**3**involving the formation of acylselonium ions**A**. Further attempts directed toward thegeneration of telluroaldehydes through a similar routestarting from <math>bis(N,N-dimethylcarbamoyl) ditelluride (**2**)<sup>2</sup> are under way in our laboratory.

## Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet. 2005.03.153.

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