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NOVEL SYNTHESIS OF 1,3,5-TRISELENANES FROM ALDEHYDES, AND NOVEL GENERATION OF SELENOALDEHYDES BY FRAGMENTATION OF 1,3,5-TRISELENANES[1)]

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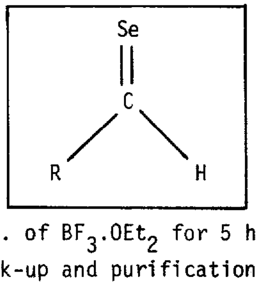
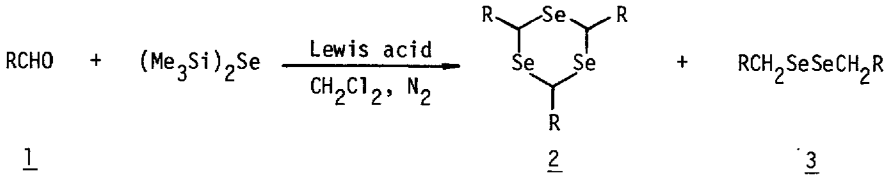
Summary : Reaction of aldehydes with $(Me_3Si)_2Se$ in the presence of Lewis acid afforded 1,3,5-triselenanes via selenoaldehydes. Novel and convenient generation of selenoaldehydes was also achieved by thermally- or Lewis acid-induced fragmentation of 1,3,5-triselenanes.

Thioaldehydes and selenoaldehydes are classified into the category of reactive intermediates containing carbon-chalcogen atom double bonds, and the clarification of their structures and reactivities is of current interest in the field of heteroatom chemistry. Several efforts have achieved the generation, trapping, or isolation of selenoaldehydes within these several years.[2-15)] However, convenient methods to generate selenoaldehydes are not fully established because most reported methods need selenium-containing precursors, the preparation of which presents some difficulty.[5-9)] Silylated chalcogenides now are recognized to be masked chalcogenide anion equivalents, and recently these reagents are widely used in the area of organic synthesis.[15-22)] In particular, such reagents show excellent utility for the synthesis of sulfur- or selenium-containing heterocycles and dialkyl chalcogenides.[18-22)] None the less, little attention has been paid to the preparation of selenocarbonyl compounds by use of the characteristic affinity of trialkylsilyl groups to carbonyl oxygen atoms.[19, 23)] Combination of bis(trialkylsilyl) selenide in the presence of Lewis acid such as $BF_3.OEt_2$ is expected to be a potential selenium-transfer reagent toward carbonyl compounds and their analogues. Actually, generation of selenoaldehydes or formation of their trimers 2 (1,3,5-triselenanes[24)]) is expected when these reagents are treated with aldehydes. 1,3,5-Triselenanes 2 also possess the cyclic acetal structure of selenoaldehydes, and is expected as well to generate selenoaldehydes 4 by retro[2+2+2]-type fragmentation. In this paper we would like to describe a convenient synthesis of 1,3,5-triselenanes 2 by the treatment of aldehydes with $(Me_3Si)_2Se$ in the presence of some Lewis acids as well as a novel generation of selenoaldehydes 4 from 1,3,5-triselenanes 2 by thermally- and Lewis acid-induced fragmentation.



General procedures of conversion from aromatic and aliphatic aldehydes to 1,3,5-triselenanes 2 are described below in the case of 2a ($R=C_6H_5$). Benzaldehyde 1a in CH_2Cl_2 was treated with 1 equiv. of $(Me_3Si)_2Se$ and 1 equiv. of $BF_3.OEt_2$ for 5 h at 0°C. The reaction mixture was then neutralized, and after the usual work-up and purification by column chromatography, compound 2 was isolated in 79% yield as the sole product. All spectral data of 2 were identical with 2,4,6-triphenyl-1,3,5-triselenane 2a reported previously by Weissflog.[24)] Reactions of several aldehydes with the reagents were also achieved in a similar manner, and all the results are given in Table 1. In every case, [4+2]-cycloadducts 5 of selenoaldehydes 4 with 2,3-dimethyl-1,3-butadiene were obtained in modest yields besides 2 when

Table 1. Preparation of 2,4,6-trisubstituted 1,3,5-triselenanes from aldehydes and $(Me_3Si)_2Se$ in the presence of Lewis acids[a)]



RCHO		Lewis acid	Temp/°C	Time/h	Yield/%[b)]	
					2	3
C_6H_5CHO	(1a)	$BF_3.OEt_2$	0	5	79	trace
C_6H_5CHO	(1a)	$SnCl_4$	R.T.	5	Complex mixture	
$4\text{-}CH_3C_6H_4CHO$	(1b)	$BF_3.OEt_2$	0	5	48	trace
$4\text{-}CH_3OC_6H_4CHO$	(1c)	$BF_3.OEt_2$	0	9	91	trace
$4\text{-}ClC_6H_4CHO$	(1d)	$BF_3.OEt_2$	0	48	33	trace
CH_3CHO	(1e)	$BF_3.OEt_2$	0	6	54	trace

a) RCHO, $(Me_3Si)_2Se$, Lewis acid : 10 mmol; CH_2Cl_2 : 40 ml.
b) Isolated yield.

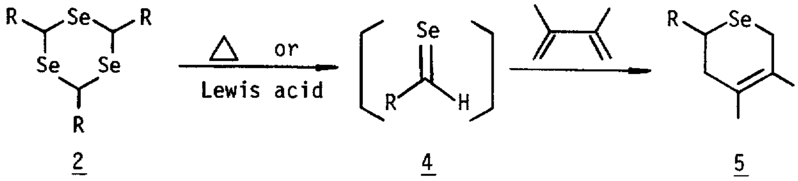
the diene was added at first to the reaction mixture. These results indicated the transient generation of selenoaldehydes 4 in the reaction media.

Fragmentation of 1,3,5-triselenanes 2 was achieved in two ways. In method A, 2 was treated with an excess amount of dienes, and the reaction mixture was heated in a sealed tube for thermal retro[2+2+2]-type fragmentation. In method B, 2 was treated with dienes in the presence of 1 equiv. of Lewis acid in a solvent at lower temperature. Reaction conditions and yields of cycloadducts are shown in Table 2, and the regioselectivities of cycloaddition of selenoaldehydes with un-symmetrical dienes (isoprene) are shown in Table 3.

From the presented results, several features of the reaction were demonstrated. Thermally-induced fragmentation of 1,3,5-triselenanes 2 generated selenoaldehydes 4, and the reaction was dramatically accelerated by soft Lewis acid such as $SnCl_4$. In every case in method B, [4+2]-cycloadducts 5 of 4 and dienes were obtained in good yields. These results suggested that coordination of selenium atom to $SnCl_4$ initiated the fragmentation of 1,3,5-triselenanes 2. When isoprene was used as diene, two cycloadducts, 6 and 7, were obtained as an isomeric mixture, and these structures were confirmed by the identification of two hydrocarbons, 8 and 9, derived from the cycloadducts, 6 and 7, by Na/liq.NH_3. Regioselectivity of cycloaddition of selenoaldehydes 4b ($R=4\text{-}CH_3C_6H_4$) with isoprene was 9:1 by method B, and 6b ($R=4\text{-}CH_3C_6H_4$) was obtained as a major product in this case. The regioselectivity observed in the reaction was fully consistent with the prediction and the experimental results of Krafft.[6)] On the other hand, cycloaddition of selenoaldehydes by thermally-induced fragmentation of 2 showed no regioselectivity.

When 2,4,6-tris(4-methoxyphenyl)-1,3,5-trithiane 10 was treated with dienes under similar conditions as shown in Table 2, 10 was quantitatively recovered in contrast with the cases of 1,3,5-triselenanes (method A). Cycloadducts of thioaldehydes were obtained in 70% yield only when 2,4,6-tris(4-methoxyphenyl)-1,3,5-trithiane 10 was heated with 2,3-dimethyl-1,3-butadiene in the

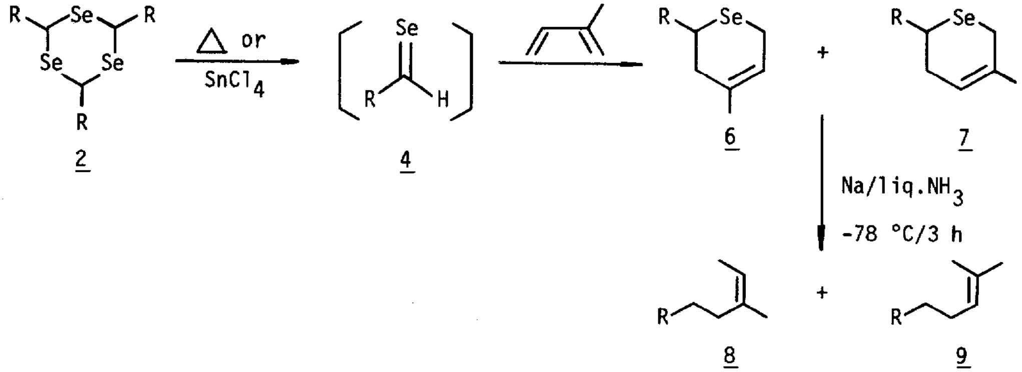
Table 2. Cycloaddition of selenoaldehydes generated from 1,3,5-triselenanes with 2,3-dimethyl-1,3-butadiene[a]



Run	Triselenane/R		Lewis acid	Solvent	Temp/°C	Time/h	Yield/% of 5[b]
1[c]	C_6H_5	(2a)	-	-	150	4	47
2[c]	4-$CH_3C_6H_4$	(2b)	-	-	150	4	60
3[c]	4-$CH_3OC_6H_4$	(2c)	-	-	150	4	60(quant.)[d]
4[c]	4-ClC_6H_4	(2d)	-	-	150	4	60(quant.)[d]
5[c]	CH_3	(2e)	-	-	180	8	57
6	C_6H_5	(2a)	$SnCl_4$	CH_2Cl_2	R.T.	16	79
7	4-$CH_3C_6H_4$	(2b)	$SnCl_4$	CH_2Cl_2	0	16	65
8	4-$CH_3OC_6H_4$	(2c)	$SnCl_4$[e]	CH_2Cl_2	0	4	trace
9	4-$CH_3OC_6H_4$	(2c)	$SnCl_4$	CH_2Cl_2	0	0.5	59
10	4-$CH_3OC_6H_4$	(2c)	$TiCl_4$	CH_2Cl_2	0	0.5	38
11	4-$CH_3OC_6H_4$	(2c)	$BF_3.OEt_2$	CH_2Cl_2	R.T.	1	22

a) Triselenane : 0.25 mmol, 2,3-dimethyl-1,3-butadiene : 6 eq., Lewis acid : 3 eq., solvent : 5 ml. b) Isolated yield. c) 2,3-dimethyl-1,3-butadiene : 25 eq., hydroquinone : 0.1 eq. d) By ^1H NMR. e) 0.3 eq.

Table 3. Cycloaddition of selenoaldehydes generated from 1,3,5-triselenanes with isoprene[a]



Triselenane/R		$SnCl_4$/eq.	Solvent	Temp/°C	Time/h	Yield/%[b] (6 + 7)	6/7
4-$CH_3C_6H_4$	(2b)	3	CH_2Cl_2	0	6	41	9/1
4-$CH_3C_6H_4$	(2b)	-[c]	THF	150	18	48	1/1
4-$CH_3OC_6H_4$	(2c)	3	CH_2Cl_2	0	0.5	34	9/1
4-$CH_3OC_6H_4$	(2c)	-[c]	THF	150	8	53	1/1

a) Triselenane : 0.5 mmol, isoprene : 6 eq., solvent : 10 ml. b) Isolated yield c) Hydroquinone : 0.1 eq.

presence of $SnCl_4$ (method B) at rather higher temperature as shown in Table 2. These differences clearly indicate the lability of 1,3,5-triselenanes in the thermally- and Lewis acid-induced fragmentation reaction.

In conclusion, formation of 1,3,5-triselenanes via the transient generation of selenoaldehydes was achieved by the treatment of aldehydes with $(Me_3Si)_2Se\text{-}BF_3.OEt_2$. Furthermore, both thermally- and Lewis acid-induced fragmentation of 1,3,5-triselenanes generated selenoaldehydes. These results demonstrated the novel synthetic utility of $(Me_3Si)_2Se$ for the synthesis of heterocyclic compounds. Further investigation on the transformation of carbonyl compounds using $(Me_3Si)_2Se$ is now in progress in our laboratory.

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