

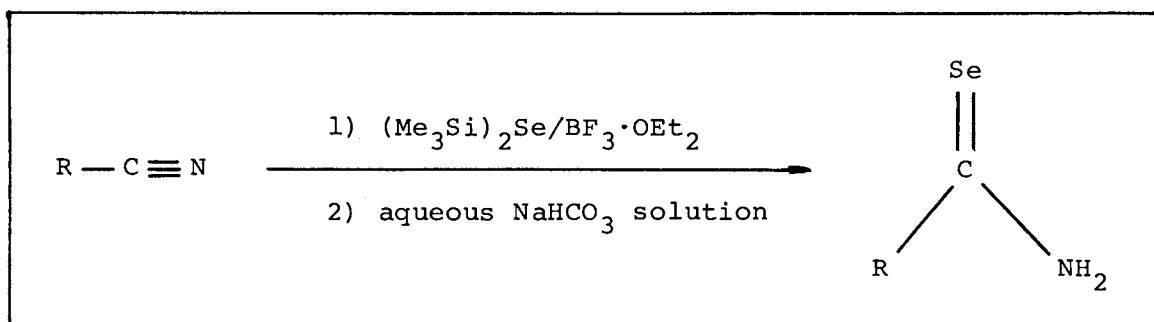
A Novel Synthesis of Primary Selenoamides from Nitriles by
the Treatment of Bis(trimethylsilyl) Selenide and $\text{BF}_3 \cdot \text{OEt}_2$

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Reaction of nitriles with $(\text{Me}_3\text{Si})_2\text{Se}$ in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ afforded the corresponding primary selenoamides in moderate yields. A selenourea and a selenothiocarbamate were also prepared in a similar manner from the corresponding cyanamide and thiocyanate.

Among the organic compounds possessing a selenocarbonyl group, primary selenoamides are regarded as novel intermediates for several types of nitrogen- and selenium-containing heterocycles.¹⁻⁵⁾ However, only a few methods for the preparation of primary selenoamides have been reported⁶⁻¹²⁾ owing to their lability toward bases and oxidants. Thus, a more effective synthesis of primary selenoamides possessing various substituents would be achieved under mild and non-basic reaction conditions. In the previous paper we described¹³⁾ a preparation of 2,4,6-trisubstituted 1,3,5-triselenanes via selenoaldehydes from the corresponding aldehydes by the use of $(\text{Me}_3\text{Si})_2\text{Se}-\text{BF}_3 \cdot \text{OEt}_2$ system and showed the novel utility for the selenating reagent of this system. In this paper we would like to describe a new method for the synthesis of primary selenoamides, a selenourea, and a selenothiocarbamate from the corresponding nitriles and their analogues by the treatment with $(\text{Me}_3\text{Si})_2\text{Se}$ and $\text{BF}_3 \cdot \text{OEt}_2$.



A typical procedure in the preparation of selenobenzamide is described as follows. To a CH_2Cl_2 solution of benzonitrile, 0.86 equiv. of $(\text{Me}_3\text{Si})_2\text{Se}$ and 2.2 equiv. of $\text{BF}_3 \cdot \text{OEt}_2$ were added under nitrogen atmosphere, and the solution was heated to 60 °C for 8 h in a sealed tube. The reaction mixture was then quenched with aqueous NaHCO_3 solution; after the usual work-up and purification by SiO_2 column chromatography, the resulting selenobenzamide was isolated as air-sensitive yellow needles in 66% yield.

In most cases no by-products except for the starting nitriles were obtained. This procedure was applied successfully to various nitriles possessing not only aromatic but also aliphatic substituents. However, $\text{N,N-dimethylcyanamide}$ $\tilde{1}$ gave three by-products besides $\text{N,N-dimethylselenourea}$ $\tilde{2}$ and the starting material $\tilde{1}$. The products were purified by SiO_2 column chromatography, and their structures were confirmed to be $\tilde{3}$, $\tilde{4}$, and $\tilde{5}$ on the basis of physical data including ^1H NMR, IR, MS, and elemental analyses.¹⁴⁾ It was plausible that the by-products, $\tilde{3}$ and $\tilde{4}$, were generated via the further condensation or oxidative dimerization¹⁵⁾ of selenourea by the reaction of $\text{BF}_3 \cdot \text{OEt}_2$. These results are shown in Table 1.

When SnCl_4 or TiCl_4 was used in place of $\text{BF}_3 \cdot \text{OEt}_2$, selenoamides were obtained in rather low yields, indicating that $\text{BF}_3 \cdot \text{OEt}_2$ was necessary for the reaction. Acceleration of the reaction by $\text{BF}_3 \cdot \text{OEt}_2$ was presumably caused by the coordination to the nitrile nitrogen as well as the trimethylsilyl group as shown in Scheme 1.

In these reactions, several points are worth noting: (1) $(\text{Me}_3\text{Si})_2\text{Se}$ reacted as a stable synthetic equivalent of hydrogen selenide by the assistance of $\text{BF}_3 \cdot \text{OEt}_2$. (2) Not only aromatic but also aliphatic nitriles afforded primary selenoamides in moderate yields under mild reaction conditions. (3) A cyanamide and a thiocyanate were also converted into the corresponding selenourea and selenothiocarbamate.

Conclusively, the combination of $(\text{Me}_3\text{Si})_2\text{Se}$ and $\text{BF}_3 \cdot \text{OEt}_2$ provided a novel and convenient synthetic method for primary selenoamides possessing various substituents.

Preparation of other selenocarbonyl compounds using the $(\text{Me}_3\text{Si})_2\text{Se}$ - $\text{BF}_3 \cdot \text{OEt}_2$ combination as well as the synthesis of selenium-containing heterocycles from primary selenoamides is now in progress in our laboratory.

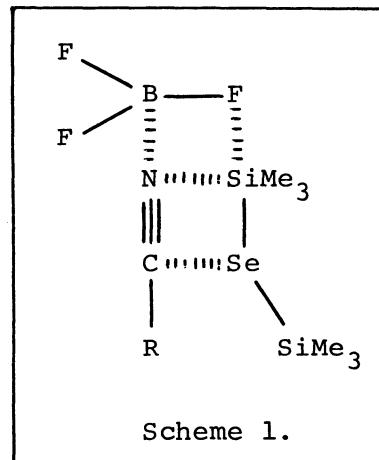
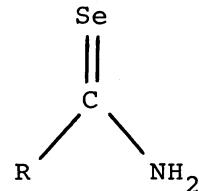


Table 1. Synthesis of Selenoamides by the Treatment of Cyano Compounds with $(\text{Me}_3\text{Si})_2\text{Se}$ in the Presence of $\text{BF}_3 \cdot \text{OEt}_2$

R — C ≡ N	1) $(\text{Me}_3\text{Si})_2\text{Se}/\text{BF}_3 \cdot \text{OEt}_2$		2) aqueous NaHCO_3 solution			
	$(\text{Me}_3\text{Si})_2\text{Se}$ /equiv.	$\text{BF}_3 \cdot \text{OEt}_2$ /equiv.	Solvent	Temp/°C	Time/h	Yield/% ^{a)}
C_6H_5	1.0	-	CH_2Cl_2	60 ^{b)}	12	0
C_6H_5	0.86	2.2	CH_2Cl_2	60 ^{b)}	8	66
C_6H_5	0.80	2.2	C_6H_6	60	12	43
$4-\text{CH}_3\text{C}_6\text{H}_4$ ¹⁶⁾	1.2	1.2	CDCl_3	reflux	2	60
$4-\text{CH}_3\text{OC}_6\text{H}_4$	1.3	1.3	CH_2Cl_2	reflux	23	40
$4-\text{ClC}_6\text{H}_4$	0.8	2.2	C_6H_6	60	40	35
CH_3	10 mmol	21 mmol	CH_3CN ^{c)}	40	40	21
$\text{CH}_3\text{CH}_2\text{CH}_2$	1.1	1.2	CH_2Cl_2	60 ^{b)}	8	79
$\text{CH}_3(\text{CH}_2)_3\text{CH}_2$	1.2	2.4	CHCl_3	reflux	3	50
$\text{CH}_3(\text{CH}_2)_5\text{CH}_2$	1.2	1.2	CHCl_3	reflux	2	50
$\text{CH}_3(\text{CH}_2)_9\text{CH}_2$	1.2	1.2	CHCl_3	reflux	9	49
$\text{C}_6\text{H}_5\text{CH}_2\text{S}$	1.2	1.2	CH_2Cl_2	r.t.	72	59
$(\text{CH}_3)_2\text{N}$	1.2	1.2	CH_2Cl_2	reflux	9	23 ^{d)}

a) Isolated yield. b) In a sealed tube. c) 3 ml. d) In the reaction with $\text{N,N-dimethylcyanamide}$ 1 , three by-products, $1,1\text{-dimethyl-2-(dimethylselenocarbamoyl)guanidine}$ 3 , $3,5\text{-bis(dimethylamino)-1,2,4-selenadiazole}$ 4 , and $2,4,6\text{-tris(dimethylamino)-1,3,5-triazine}$ 5 were obtained in 9, 21, and 17% yields, respectively.

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- 14) 3 : Colorless needles, mp 122-122.5 °C (Et₂O), MS(m/e) ; 222(M⁺, bp), 220(M⁺, 71%), 178(M⁺-NMe₂, 36%), IR(KBr) ; 3300, 3040, 2900, 1610, 1545, 1485, 1425, 1403, 1380, 1345, 1260, 1208, 1108, 1050, 1003, 730 cm⁻¹, ¹H NMR(CDCl₃) ; δ 3.03(6H, s), 3.22(3H, s), 3.51(3H, s), 7.47(2H, br.s), Found ; C, 32.43, H, 6.40, N, 26.05%, Calcd for C₆H₁₄N₄Se ; C, 32.58, H, 6.38, N, 25.33%.
- 4 : Colorless needles, mp 49-50 °C (Hexane), MS(m/e) ; 220(M⁺, 99%), 218(M⁺, 84%), 176(M⁺-NMe₂, 98%), 148(M⁺-Me₂NCN, bp), 70(Me₂NCN, 97%), IR(KBr) ; 2910, 2850, 1590, 1510, 1370, 1330, 1250, 1190, 1110, 1050, 1020, 850 cm⁻¹, ¹H NMR(CDCl₃) ; δ 3.08(6H, s), 3.11(6H, s).
- 15) 3,5-Bis(dimethylamino)-1,2,4-selenadiazole 4 was obtained in 31% yield by the treatment of N,N-dimethylselenourea 2 with 1.1 equiv. of I₂ in MeOH at 0 °C for 10 min followed by the work-up using NH₄OH solution.
- 16) Although a new signal (δ 0.45 ppm) tentatively assigned to be a trimethylsilyl group of N,N-bis(trimethylsilyl)-4-methylselenobenzamide was observed in the ¹H NMR spectrum of the reaction mixture, the structure of the intermediate was not confirmed from the result.

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