CHEMISTRY LETTERS, pp. 1403-1406, 1990.

A Novel Synthesis of Primary Selenoamides from Nitriles by the Treatment of Bis(trimethylsilyl) Selenide and $BF_3 \cdot OEt_2$

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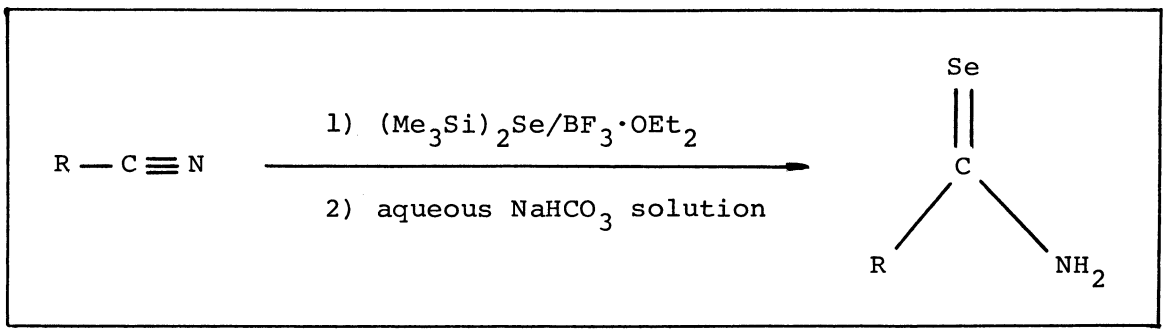
Reaction of nitriles with $(Me_3Si)_2Se$ in the presence of $BF_3 \cdot OEt_2$ afforded the corresponding primary selenoamides in moderate yields. A selenourea and a selenothiocarbamate were also prepared in a similar manner from the corresponding cyanamide and thiocyanate.

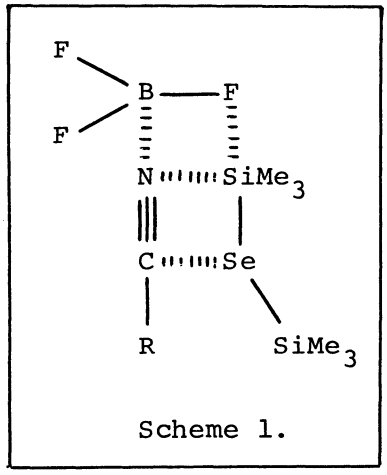
Among the organic compounds possessing a selenocarbonyl group, primary selenoamides are regarded as novel intermediates for several types of nitrogen- and selenium-containing heterocycles.[1-5] However, only a few methods for the preparation of primary selenoamides have been reported[6-12] owing to their 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 described[13] a preparation of 2,4,6-trisubstituted 1,3,5-triselenanes via selenoaldehydes from the corresponding aldehydes by the use of $(Me_3Si)_2Se$-$BF_3 \cdot OEt_2$ 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 $(Me_3Si)_2Se$ and $BF_3 \cdot OEt_2$.



A typical procedure in the preparation of selenobenzamide is described as follows. To a CH_2Cl_2 solution of benzonitrile, 0.86 equiv. of $(Me_3Si)_2Se$ and 2.2 equiv. of $BF_3 \cdot OEt_2$ 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, N,N-dimethylcyanamide 1 gave three by-products besides N,N-dimethylselenourea 2 and the starting material 1. The products were purified by SiO_2 column chromatography, and their structures were confirmed to be 3, 4, and 5 on the basis of physical data including ^1H NMR, IR, MS, and elemental analyses.[14] It was plausible that the by-products, 3 and 4, were generated via the further condensation or oxidative dimerization[15] of selenourea by the reaction of $BF_3 \cdot OEt_2$. These results are shown in Table 1.

When $SnCl_4$ or $TiCl_4$ was used in place of $BF_3 \cdot OEt_2$, selenoamides were obtained in rather low yields, indicating that $BF_3 \cdot OEt_2$ was necessary for the reaction. Acceleration of the reaction by $BF_3 \cdot OEt_2$ was presumably caused by the coordination to the nitrile nitrogen as well as the trimethylsilyl group as shown in Scheme 1.



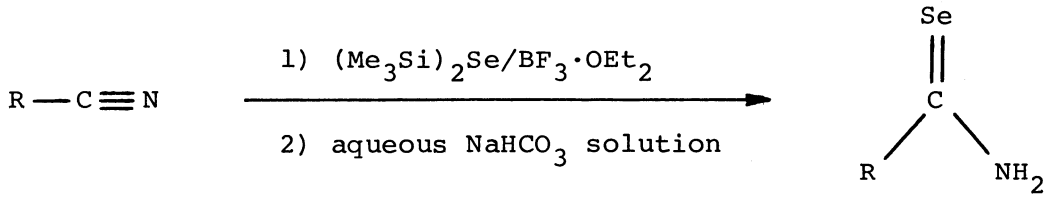
Scheme 1.

In these reactions, several points are worth noting: (1) $(Me_3Si)_2Se$ reacted as a stable synthetic equivalent of hydrogen selenide by the assistance of $BF_3 \cdot OEt_2$. (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 $(Me_3Si)_2Se$ and $BF_3 \cdot OEt_2$ provided a novel and convenient synthetic method for primary selenoamides possessing various substituents.

Preparation of other selenocarbonyl compounds using the $(Me_3Si)_2Se$-$BF_3 \cdot OEt_2$ 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 $(Me_3Si)_2Se$ in the Presence of $BF_3 \cdot OEt_2$



R	$(Me_3Si)_2Se$ /equiv.	$BF_3 \cdot OEt_2$ /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
$4\text{-}CH_3C_6H_4$[16]	1.2	1.2	$CDCl_3$	reflux	2	60
$4\text{-}CH_3OC_6H_4$	1.3	1.3	CH_2Cl_2	reflux	23	40
$4\text{-}ClC_6H_4$	0.8	2.2	C_6H_6	60	40	35
CH_3	10 mmol	21 mmol	CH_3CN[c]	40	40	21
$CH_3CH_2CH_2$	1.1	1.2	CH_2Cl_2	60[b]	8	79
$CH_3(CH_2)_3CH_2$	1.2	2.4	$CHCl_3$	reflux	3	50
$CH_3(CH_2)_5CH_2$	1.2	1.2	$CHCl_3$	reflux	2	50
$CH_3(CH_2)_9CH_2$	1.2	1.2	$CHCl_3$	reflux	9	49
$C_6H_5CH_2S$	1.2	1.2	CH_2Cl_2	r.t.	72	59
$(CH_3)_2N$	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 N,N-dimethylcyanamide 1, three by-products, 1,1-dimethyl-2-(dimethylselenocarbamoyl)guanidine 3, 3,5-bis(dimethylamino)-1,2,4-selenadiazole 4, and 2,4,6-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 (Et_2O), MS(m/e) ; 222(M^+, bp), 220(M^+, 71%), 178(M^+-NMe_2, 36%), IR(KBr) ; 3300, 3040, 2900, 1610, 1545, 1485, 1425, 1403, 1380, 1345, 1260, 1208, 1108, 1050, 1003, 730 cm^{-1}, ^1H NMR($CDCl_3$) ; 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 $C_6H_{14}N_4Se$; 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^+-NMe_2, 98%), 148(M^+-Me_2NCN, bp), 70(Me_2NCN, 97%), IR(KBr) ; 2910, 2850, 1590, 1510, 1370, 1330, 1250, 1190, 1110, 1050, 1020, 850 cm^{-1}, ^1H NMR($CDCl_3$) ; 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 I_2 in MeOH at 0 °C for 10 min followed by the work-up using NH_4OH 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.

(Received May 21, 1990)