Conversion of Amides, *N,N,N′,N′*-Tetramethylurea, and Esters to the Corresponding Selenoxo Compounds by Treatment with Bis(trimethylsilyl) Selenide and $BF_3 \cdot OEt_2$

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Synopsis. The reactions of amides and *N,N,N′,N′*-tetramethylurea with $(Me_3Si)_2Se$ in the presence of $BF_3 \cdot OEt_2$ afforded the corresponding slelenoxo compounds in good yields. On the other hand, selenation of ethyl and butyl benzoates in a similar manner gave benzoin and 2,3,5,6-tetraphenyl-1,4-diselenin via selenoesters. The trapping of selenoesters was also achieved by 2,3-dimethyl-1,3-butadiene to afford [4+2] cycloadducts.

Recently, a convenient conversion of carbonyl compounds to the corresponding selenoxo compounds has been achieved by the use of various selenating reagents possessing reactive metal-selenium bonds.[1—7] However, limited methods for the selenation of carboxylic acid derivatives have been provided in spite of the potential of selenoesters, selenoamides, and selenoureas as precursors of various selenium-containing heterocycles. On the other hand, we previously reported that the treatment of $(Me_3Si)_2Se$ (**1**) and Lewis acids was effective for the synthesis of selenoaldehydes.[4] It was thus naturally expected that the selenation of carboxylic acid derivatives could also be achieved in a similar manner. In this paper we describe a novel synthesis of selenoamides, selenourea, and selenoesters by treating carbonyl compounds with **1** and $BF_3 \cdot OEt_2$ at elevated temperature.

N-Methylbenzamide (**2d**), *N,N*-dialkylamides (**2a**—**c**, **2f**—**g**), and *N,N,N′,N′*-tetramethylurea (**2h**) were treated with 2 molar amounts of $(Me_3Si)_2Se$ (**1**) and 1 molar amount of $BF_3 \cdot OEt_2$ in benzene at 100—150 °C in an autoclave; the corresponding selenoxo compounds **3** were isolated in high to modest yields in all cases. However, benzamide (**2e**) was inert to the reaction, and the starting amide was recovered after the treatment of reagent **1** and $BF_3 \cdot OEt_2$, even under rather drastic reaction conditions.[8] The structures of the resulting selenoamides **3** and *N,N,N′,N′*-tetremethylselenourea (**3h**) were confirmed by MS, IR, ^1H NMR, and elemental analysis, and by a comparison of their physical properties with those reported by Rae[9] and Jensen.[10] Table 1 shows all of results of the reactions.

Unexpectedly, the treatment of ethyl and butyl benzoates (**4** and **5**) with reagent **1** and $BF_3 \cdot OEt_2$ in an autocleave in a similar manner afforded benzoin (**7**) (6 and 11% yields, respectively) and 2,3,5,6-tetraphenyl-1,4-diselenin (**9**) (25 and 15% yields, respectively); isolation of the corresponding selenoesters **6** was not successful in both cases. The trapping of **6** was achieved by carrying out the selenation reaction of **4** and **5** in the presence of 2,3-dimethyl-1,3-butadiene to afford 3,4-dimethyl-6-phenyl-2*H*-selenin (**8**) in 17 and 63% yields from ethyl and butyl benzoates (**4** and **5**), respectively. It was assumed that compound (**8**) was generated by a Lewis acid-induced elimination of alkoxyl groups from the [4+2] cycloadducts.

It is already known that selenoesters undergo deselenative dimerization to give enol ethers at high temperature by the assistance of PEt_3.[11] Thus, our results also suggested that the selenoesters **6** were generated in the reaction mixture and were converted to benzoin through the formation of enol ethers followed by hydrolysis under an acidic reaction condition. However, the mechanism for the formation of **9** remained unknown, and the deselenative dimerization of some unusual intermediate, such as benzenecarbodiselenoic anhydroselenide **A**, afforded by a $(Me_3Si)_2Se$-assisted substitution of the alkoxyl group of selenoester **6** to the selenium atom (as reported by Segi et al.[6]), was supposed to give **9**, as shown in Scheme 1. However, all efforts to detect or trap such an intermediate **A** were unsuccessful.[12]

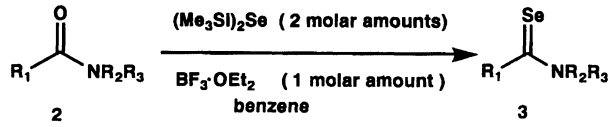
Experimental

Materials. The amides, *N,N,N′,N′*-tetramethylurea, and the esters were commercially available and purified by either distillation or recrystallization before use. Boron trifluoride etherate and 2,3-dimethyl-1,3-butadiene were commercial reagent-grade materials, and were purified by distillation before use. $(Me_3Si)_2Se$ (**1**) was prepared according to the literature.[13] All of the solvents were dried over appropriate drying agents and freshly distilled before use.

Instruments. The IR spectra were recorded for thin films (neat) or KBr disks on a JASCO FT/IR-7300 infrared spectrophotometer. The ^1H NMR spectra were measured with a Hitachi R-22 (90 MHz) spectrometer in a $CDCl_3$ solution containing tetremthylsilane (TMS) as an internal standard. The mass spectra were recorded with a Hitachi M-2000 spectrometer with electron impact ionization at 20 or 70 eV using a direct inlet system. Elemental analyses were performed with a Yanagimoto MT-3 CHN Analyzer.

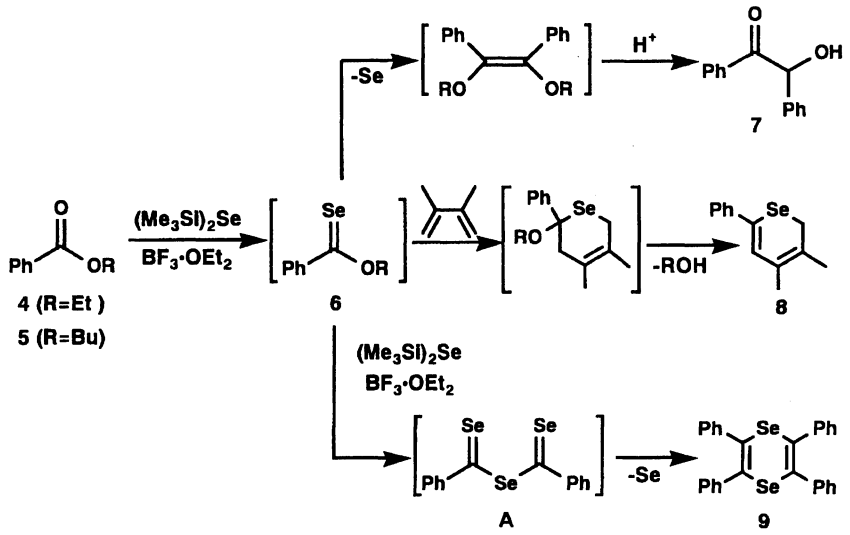
General Procedure for the Reaction of Amides, *N,N,N′,N′*-Tetramethylurea, or Esters with $(Me_3Si)_2Se$ and $BF_3 \cdot OEt_2$. To a 50 ml benzene solution of $(Me_3Si)_2Se$ (2.12 g, 9.4 mmol) and *N,N*-dimethylbenzamide (**2c**) (700 mg, 4.7 mmol) was added a 5 ml benzene solution of $BF_3 \cdot OEt_2$ (666 mg, 4.7 mmol); the reaction mixture was heated to 100 °C for 4 h in an autoclave. After treating with an aqueous $NaHCO_3$ solution, the reaction mixture was extracted with CH_2Cl_2. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated

Table 1. Syntheses of Selenoamides and *N,N,N′,N′*-Tetramethylselenourea



Entry	Substrate				Temp	Time	Yield[a]
	R_1	R_2	R_3		°C	h	% of **3**
1	H	CH_3	CH_3	(**2a**)	150	2	74
2	CH_3	CH_3	CH_3	(**2b**)	150	15	56
3	C_6H_5	CH_3	CH_3	(**2c**)	100	6	73
4	C_6H_5	CH_3	H	(**2d**)	150	17	34
5	C_6H_5	H	H	(**2e**)	150	24	Trace[b]
6	$-(CH_2)_3-$		CH_3	(**2f**)	120	6	89
7	$C_6H_5CH=CH$	CH_3	CH_3	(**2g**)	120	5	49
8	$(CH_3)_2N$	CH_3	CH_3	(**2h**)	150	24	64

a) Isolated yields. b) Recovery of substrate.



Scheme 1.

in vacuo. Purification of the crude orange oil by column chromatography on silica gel gave *N,N*-dimethylselenobenzamide (**3c**) (727 mg, 73%) as yellow needles.

***N,N*-Dimethylselenoformamide (3a).** Orange oil; MS *m/z* 137 (M^+, ^{80}Se); IR (neat) 1540 cm^{-1} (lit,[14] 1540 cm^{-1}); ^1H NMR ($CDCl_3$) δ=3.32 (3H, s), 3.36 (3H, s), and 10.60 (1H, s), (lit,[14] δ=10.62); UV ($CHCl_3$) λ_{max} 299.5, 396.5 nm (lit,[14] λ_{max} 301, 400 nm).

***N,N*-Dimethylselenoacetamide (3b).** Yellow needles; mp 77 °C (lit,[9] 83—84 °C).

***N,N*-Dimethylselenobenzamide (3c).** Orange needles; mp 76—77 °C (lit,[9] 79—80 °C).

***N*-Methylselenobenzamide (3d).** Yellow plates; mp 102—103 °C (lit,[9,10] 104—105 °C).

Selenobenzamide (3e). Yellow needles; mp 125 °C (lit,[15] 125 °C).

***N*-Methylpyrrolidine-2-selone (3f).** Yellow needles; mp 33 °C (lit,[9] 29—30 °C).

***N,N*-Dimethylselenocinnamamide (3g).** Red crystals; mp 88—89 °C; MS *m/z* 239 (M^+, 38%, ^{80}Se); IR (neat) 1615, 1510, 1390, 1312, 1275, 1255, 1108, 975, 745, and 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.36 (3H, s), 3.68 (3H, s), 6.97 (1H, d, J=15 Hz), 7.21—7.60 (5H, m), and 7.83 (1H, d, J=15 Hz). Found: C, 55.10; H, 5.47; N, 5.68%. Calcd for $C_{11}H_{13}NSe$: C, 55.47; H, 5.50; N, 5.88%.

***N,N,N′,N′*-Tetramethylselonourea (3h).** Yellow needles; mp 78—79 °C (lit,[16] 79—80 °C).

Reaction of Butyl Benzoate (5) with $(Me_3Si)_2Se$ and BF_3·OEt_2 in the Presence of 2,3-Dimethyl-1,3-butadiene. To a 5 ml benzene solution of butyl benzoate (1.78 g, 10 mmol), $(Me_3Si)_2Se$ (4.50 g, 20 molar amounts), and 2,3-dimethyl-1,3-butadiene (4.10 g, 4 molar amounts) was added a 5 ml benzene solution of BF_3·OEt_2 (2.84 g, 2 molar amounts); the reaction mixture was heated at 150 °C for 5 h in an autoclave. After treating with an aqueous $NaHCO_3$ solution, the reaction mixture was extracted with CH_2Cl_2. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification of the crude product by column chromatography on alumina by using hexane as an eluent gave 3,4-dimethyl-6-

phenyl-2*H*-selenin (**8**) (1.56 g, 63%).

3,4-Dimethyl-6-phenyl-2*H*-selenin (8). Yellow oil; MS *m/z* 250 (M^+, 76%, ^{80}Se); IR (neat) 3076, 3055, 3017, 2912, 2858, 1595, 1488, 1443, 1229, 1090, 759, and 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.82—1.98 (6H, m), 3.28 (2H, br. s), 6.50 (1H, s), and 7.22—7.63 (5H, m). Found: C, 62.41; H, 5.76%. Calcd for $C_{13}H_{14}Se$: C, 62.65; H, 5.66%.

2,3,5,6-Tetraphenyl-1,4-diselenin (9). Colorless needles, mp 223.5—224.0 °C; MS *m/z* 516 (M^+, 2%, ^{80}Se); IR (KBr) 1596, 1483, 1440, 1070, 1031, 794, 761, 720, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.15 (20H, br. s). Found: C, 65.35; H, 3.84%. Calcd for $C_{28}H_{20}Se_2$: C, 65.38; H, 3.92%.

Birch Reduction of 2,3,5,6-Tetraphenyl-1,4-diselenin (9). 50 ml of liq NH_3 was treated with sodium metal (45 mg, 30 molar amounts) at −50 °C; subsequently, 10 ml of a THF solution of 2,3,5,6-tetraphenyl-1,4-diselenin (**9**) (30 mg, 0.058 mmol) was added dropwise to the solution. The reaction mixture was stirred at −50 °C for 1 h under a nitrogen atmosphere. The reaction mixture was quenched by ammonium chloride (1.05 g), and extracted with benzene. The organic layer was dried over anhydrous Na_2SO_4 and concentrated by evaporation; the residue was then purified by column chromatography on silica gel by using benzene as an eluent to give 1,2-diphenylethane (18 mg, 85%) as a sole product.

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