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Synthesis Utilizing Reducing Ability of Carbon Monoxide: A New Method for Selective Synthesis of Diorganyl Selenides and Diselenides Using a Selenium–Carbon Monoxide–Water Reaction System

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A new approach to the synthesis of diorganyl selenides and diselenides is described. Selective generation of tertiary amine salts of hydrogen selenide ($[HSe^-]\cdot[R_3NH^+]$) and hydrogen diselenide ($[HSe_2^-]\cdot[R_3NH^+]$) has been achieved by controlling the reaction conditions for the reduction of elemental selenium with carbon monoxide and water in the presence of tertiary amine. Subsequent alkylation provided a wide variety of symmetrical dialkyl selenides (R_2Se) and diselenides (R_2Se_2) with a high degree of selectivity. Acylation of the amine salt of hydrogen selenide by equimolar amounts of acid chlorides led to the formation of tertiary amine salt of selenocarboxylates $[R_3NH^+]\cdot[RCOSe^-]$ in excellent yields. Further acylation and alkylation of this salt yielded bis(acyl) selenides $[(RCO)_2Se]$ and *Se*-alkyl selenocarboxylates ($RCOSeR'$), respectively. Moreover, oxidation of the amine salt of selenocarboxylates gave rise to bis(acyl) diselenides $[(RCO)_2Se_2]$.

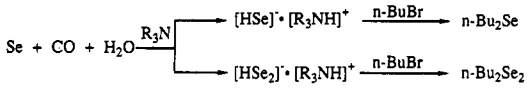
Carbon monoxide has been widely employed as a useful reducing agent[1] in organic synthesis. For example, there exist numerous papers to date of the transition metal catalyzed reduction or reductive carbonylation of various organic compounds with carbon monoxide and water.[2]

Recently we have found that elemental selenium can be readily reduced by carbon monoxide and water in the presence of tertiary amine to produce an amine salt of hydrogen selenide ($[HSe^-]\cdot[R_3NH^+]$),[3] which can be regarded as an excellent reagent for introducing selenium functions into organic molecules.[4] In this paper, we report a new approach for the selective synthesis of diorganyl selenides and diselenides by using $Se/CO/H_2O$ reaction system.

Results and Discussion

In the organic chemistry of selenium, the key intermediate compounds are often diorganyl selenides and diselenides, and much effort is being devoted to accomplish the preparation of these compounds.[5] One of the most straightforward access to these compounds is the alkylation of selenolate anions (Se^{2-} and Se_2^{2-}).[6] We have investigated the reduction of elemental selenium with carbon monoxide and water in detail and have discovered that the amine salts of H_2Se and H_2Se_2 can be generated selectively by controlling the reaction conditions.

Scheme I



(i) Synthesis of Dialkyl Selenides and Diselenides. To establish the proper conditions where either of the selenolate anions (HSe^- or HSe_2^-) can be formed exclusively, the reduction of selenium with carbon monoxide and water was examined under several reaction conditions. The species formed in situ was alkylated with butyl bromide (Scheme I), and the results are shown in Table I. The nature of tertiary amine showed marked effect on the ratio of selenide and diselenide: strongly basic amine such as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) was the most efficient for the formation of selenide (run 7), whereas the use of weaker tertiary amine such as triethylamine or *N*-methylpyrrolidine afforded diselenide exclusively (runs 1–3). The product distribution was also affected by the pressure of carbon monoxide, reaction time, and reaction temperature (runs 3–6): higher pressure and longer reaction time led to the preferential formation of selenide. These results are understandable by taking into account the reduction of elemental selenium to HSe^- proceeds via HSe_2^- as an intermediate, and the reduction can be stopped cleanly at the desired HSe_2^- stage under controlled reaction conditions.

Encouraged by these observations, selective synthesis of various dialkyl selenides and diselenides was examined by use of several alkyl halides. Dialkyl selenides were prepared in good yields with an excellent selectivity by the conducting reaction at 80 °C for 1 h under the pressure of CO (5 atm) in the presence of DBU, followed by alkylation (Table II). It was described in the literature that the alkylation of alkali metal salts of H_2Se with secondary alkyl halides hardly proceeded.[6] In contrast, the amine

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[1] For recent reviews: (a) Ford, P. C. *Acc. Chem. Res.* **1981**, *14*, 31. (b) King, A. D., Jr.; King, R. B.; Yang, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 1028. (c) Bricker, J. C.; Nagel, C. C.; Shore, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 1444. (d) Walker, H. W.; Pearson, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1983**, *105*, 1179. (e) Kang, H. C.; Mauldin, C. H.; Cole, T.; Slegeir, W.; Cann, K.; Pettit, R. *J. Am. Chem. Soc.* **1977**, *99*, 8323. (f) Choudhury, D.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1885. (g) Kelly, J. K.; Vos, J. G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 628. (h) Murata, K.; Matsuda, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2089. (i) Watanabe, Y.; Suzuki, N.; Tsuji, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2445. (j) Prent, E. *ACS Symposium Ser.* **1987**, *328*, 154. (k) Rizkallc, N.; Goliaszewski, A. *ACS Symposium Ser.* **1987**, *328*, 136. (l) Wegman, P. W.; Busby, D. C.; Letts, J. B. *ACS Symposium Ser.* **1987**, *328*, 125.

[2] See for examples: (a) Cann, K.; Cole, T.; Slegeir, W.; Pettit, R. *J. Am. Chem. Soc.* **1978**, *100*, 3969. (b) Alper, H.; Amaratunga, S. *Tetrahedron Lett.* **1980**, *21*, 2603. (c) Watanabe, Y.; Tsuji, Y.; Ohsumi, T.; Takeuchi, R. *Tetrahedron Lett.* **1983**, *24*, 4121. (d) Bremer, J.; Dexheimer, V.; Madeja, K. *J. Prakt. Chem.* **1981**, *323*, 857. (e) Kitamura, T.; Joh, T.; Hagihara, N. *Chem. Lett.* **1975**, 203. (f) Watanabe, Y.; Tsuji, Y.; Ohsumi, T.; Takeuchi, R. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2867. (g) Minkov, A. I.; Frenenko, N. K.; Efjmov, O. A. *Dokl. Akad. Nauk. SSSR* **1985**, *283*, 160; *Chem. Abstr.* **1986**, *105*, 6243q.

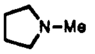
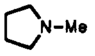
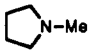
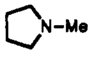
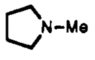
[3] Sonoda, N.; Kondo, K.; Nagano, K.; Kambe, N.; Morimoto, F. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 308.

[4] Synthesis of organic selenium compounds using $Se–CO–H_2O$ reaction system, see: (a) Ogawa, A.; Miyake, J.; Karasaki, S.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1985**, *50*, 384. (b) Ogawa, A.; Miyake, J.; Kambe, N.; Murai, S.; Sonoda, N. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1448. (c) Nishiyama, Y.; Hamanaka, S.; Ogawa, A.; Murai, S.; Sonoda, N. *Synth. Commun.* **1986**, *16*, 1059.

[5] Gladysz, J. A.; Hornby, J. L.; Garbe, J. E. *J. Org. Chem.* **1978**, *43*, 1204 and references therein.

[6] Thompson, D. P.; Boudjouk, P. *J. Org. Chem.* **1988**, *53*, 2109 and references therein.

Table I. Selectivity of Hydrogen Selenide/Diselenide under Several Reaction Conditions[a]

run	base (mmol)	temp, °C	CO, atm	time, h	yield,[b,c] %	
					n-Bu_2Se	n-Bu_2Se_2
1	Et_3N (15)	80	5	1	0	59
2	 (5)	80	5	1	0	48
3	 (15)	80	5	1	0	78
4	 (15)	80	30	1	70	9
5	 (15)	80	5	5	63	8
6	 (15)	100	5	1	30	46
7	DBU (15)	80	5	1	78	0

[a] Reaction conditions: Se (5 mmol), water (15 mmol), CH_3CN (5 mL), n-BuBr (25 mmol). [b] Based on selenium. [c] GLC yield.

Table II. Synthesis of Dialkyl Selenides[a]

$$\underset{5\text{ mmol}}{\text{Se}} + \underset{5\text{ atm}}{\text{CO}} + \underset{15\text{ mmol}}{\text{H}_2\text{O}} \xrightarrow[\substack{\text{CH}_3\text{CN (5 mL)}\\ 80\ ^\circ\text{C, 1h}}]{\text{DBU (15 mmol)}} \xrightarrow[\substack{80\ ^\circ\text{C, 1 h}\\ \text{in N}_2}]{\text{RX (25 mmol)}} \text{R}_2\text{Se}$$

run	alkyl halide	selenide	yield,[b,c] %
1	n-C_4H_9Cl	(n-$C_4H_9)_2Se$ (**1**)	75
2	n-C_4H_9Br	**1**	78
3	n-C_4H_9I	**1**	82
4	i-C_4H_9Br	(i-$C_4H_9)_2Se$ (**2**)	70
5	s-C_4H_9Br	(s-$C_4H_9)_2Se$ (**3**)	74
6	n-$C_6H_{13}Br$	(n-$C_6H_{13})_2Se$ (**4**)	75
7	$C_6H_5CH_2Br$	$(C_6H_5CH_2)_2Se$ (**5**)	62

[a] All reactions were performed on a 5-mmol scale according to the procedure described in the Experimental Section. [b] Based on selenium. [c] Isolated yield.

salt of hydrogen selenide easily underwent alkylation with secondary alkyl halides to provide corresponding selenides in good yields (run 5).

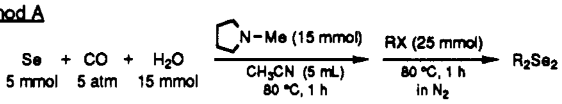
On the other hand, the use of N-methylpyrrolidine instead of DBU as the base permitted the predominant formation of diselenides (method A in Table III). In addition, an alternative method for the synthesis of diselenides has been developed on the basis of the reaction of hydrogen selenide anion (HSe^-) with equimolar amounts of elemental selenium. The generation of HSe_2^- was accomplished by addition of selenium (1 equiv) to the reaction mixture containing HSe^- (which was generated from Se, CO, and H_2O under a similar conditions as described in run 7 in Table I). The alkylation of HSe_2^- then provided dialkyl diselenides in good yields (eq 1 and method B in Table III).

$$[\text{HSe}]^-\cdot[\text{DBU}\cdot\text{H}]^+ \xrightarrow{\text{Se}} [\text{HSe}_2]^-\cdot[\text{DBU}\cdot\text{H}]^+ \xrightarrow{\text{RX}} (\text{RSe}\!-\!)_2 \quad (\text{eq. 1})$$

(ii) Synthesis of Bis(acyl) Selenides and Diselenides. Bis(acyl) selenides and diselenides are synthetically promising reagents for introducing acyl function into organic molecules.[7] Nonetheless, only very limited methods have been developed for the selective formation of bis(acyl) selenides and diselenides.[7a,8] Thus, the possibility of the selective synthesis of bis(acyl) selenides and diselenides was investigated by the reaction of selenolate anions (HSe^- or HSe_2^-) with acyl chlorides. To avoid the hydrolysis of acyl chlorides, the reduction of selenium to selenolate anion (HSe^-) was performed by using a stoichiometric amount of water. Subsequent acylation of HSe^- with acyl chlorides provided bis(acyl) selenides (**11** and **12**) in high yields (eq 2).

Table III. Synthesis of Dialkyl Diselenides[a]

Method A

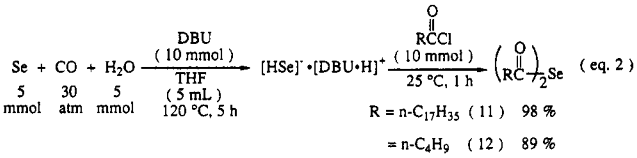


Method B

$$\underset{5\text{ mmol}}{\text{Se}} + \underset{5\text{ atm}}{\text{CO}} + \underset{15\text{ mmol}}{\text{H}_2\text{O}} \xrightarrow[\substack{\text{CH}_3\text{CN (5 mL)}\\ 80\ ^\circ\text{C, 1 h}}]{\text{DBU (–10 mmol)}} \xrightarrow[\substack{80\ ^\circ\text{C, 1 h}\\ \text{in N}_2}]{\text{Se (5 mmol)}} \xrightarrow[\substack{80\ ^\circ\text{C, 1 h}\\ \text{in N}_2}]{\text{RX (20 mmol)}} \text{R}_2\text{Se}_2$$

run	alkyl halide	diselenide	yield,[b,c] %	
			method A	method B
1	n-C_5H_9Br	(n-$C_4H_9Se)_2$ (**6**)	78	85
2	i-C_4H_9Br	(i-$C_4H_9Se)_2$ (**7**)	70	71
3	s-C_4H_9Br	(s-$C_4H_9Se)_2$ (**8**)	84	77
4	n-$C_6H_{13}Br$	(n-$C_6H_{13}Se)_2$ (**9**)	80	77
5	$C_6H_5CH_2Br$	$(C_6H_5CH_2Se)_2$ (**10**)	70[d]	75

[a] All reactions were performed on a 5-mmol scale according to the procedure described in the Experimental Section. [b] Based on selenium. [c] Isolated yield. [d] Involving the formation of dibenzyl selenide (18%).

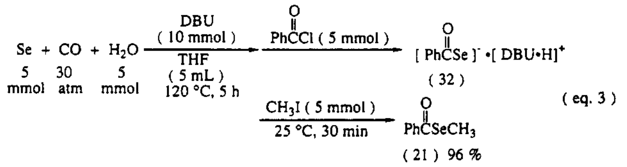


$$\underset{\substack{5\\ \text{mmol}}}{\text{Se}} + \underset{\substack{30\\ \text{atm}}}{\text{CO}} + \underset{\substack{5\\ \text{mmol}}}{\text{H}_2\text{O}} \xrightarrow[\substack{\text{THF}\\ \text{(5 mL)}\\ 120\ ^\circ\text{C, 5 h}}]{\substack{\text{DBU}\\ \text{(10 mmol)}}} [\text{HSe}]^-\cdot[\text{DBU}\cdot\text{H}]^+ \xrightarrow[25\ ^\circ\text{C, 1 h}]{\substack{\text{RC(=O)Cl}\\ \text{(10 mmol)}}} (\text{RC(=O)}\!-\!)_2\text{Se} \quad (\text{eq. 2})$$

$\text{R} = \text{n-C}_{17}\text{H}_{35}$ (**11**) 98 %

$= \text{n-C}_4\text{H}_9$ (**12**) 89 %

In contrast to acyl chlorides, aroyl chlorides such as benzoyl chloride did not produce bis(benzoyl) selenide, and instead benzoic acid was obtained in 85% yield after aqueous workup. To gain further insight into the details of the present transformation, the model reaction was monitored by the ^{13}C and ^{77}Se NMR spectra. When HSe^-, generated in situ, was treated with equimolar amounts of benzoyl chloride, a peak assigned to the carbonyl carbon of benzoyl chloride (δ 168.7) disappeared, and a new peak appeared at δ 177.0. Quenching of the reaction mixture with methyl iodide at this stage led to the formation of Se-methyl benzeneselenoate (**21**) in 96% yield (eq 3). This



$$\underset{\substack{5\\ \text{mmol}}}{\text{Se}} + \underset{\substack{30\\ \text{atm}}}{\text{CO}} + \underset{\substack{5\\ \text{mmol}}}{\text{H}_2\text{O}} \xrightarrow[\substack{\text{THF}\\ \text{(5 mL)}\\ 120\ ^\circ\text{C, 5 h}}]{\substack{\text{DBU}\\ \text{(10 mmol)}}} \xrightarrow{\text{PhC(=O)Cl (5 mmol)}} \underset{(\ 32\ )}{[\text{PhC(=O)Se}]^-\cdot[\text{DBU}\cdot\text{H}]^+} \xrightarrow[25\ ^\circ\text{C, 30 min}]{\text{CH}_3\text{I (5 mmol)}} \underset{(\ 21\ )\ 96\ \%}{\text{PhC(=O)SeCH}_3} \quad (\text{eq. 3})$$

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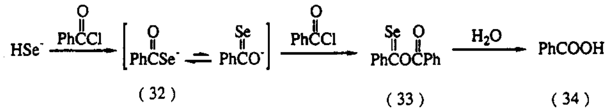
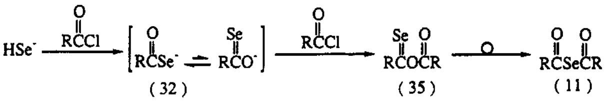
[7] (a) Ishihara, H.; Sato, S.; Hirabayashi, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3007. (b) Ishihara, H.; Muto, S.; Kato, S. *Synthesis* **1986**, 128. (c) Fujiwara, S.; Ogawa, A.; Kambe, N.; Ryu, I.; Sonoda, N. *Tetrahedron Lett.* **1988**, *29*, 6121. (d) Nishiyama, Y.; Katsuura, A.; Okamoto, Y.; Hamanaka, S. *Chem. Lett.* **1989**, 1825.

[8] (a) Jensen, A.; Böja, L.; Henriksen, H. *Acta Chem. Scand.* **1972**, *26*, 1465. (b) Szperl, L.; Wiorogorshy, L. *Org. Prep. Proc. Int.* **1978**, *10*, 289.

Scheme II



Scheme III

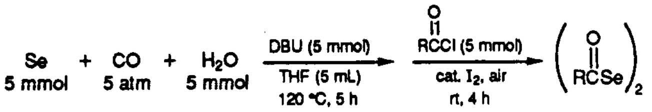


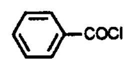
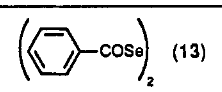
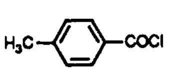
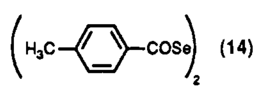
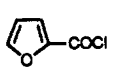
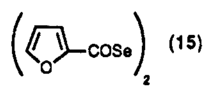
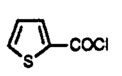
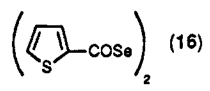
supports the existence of the amine salts of selenobenzoic acid (**32**) in the mixture resulting from aroylation of HSe^-.[9,10] Addition of 1 more equiv of benzoyl chloride to the solution containing **32** resulted in disappearance of a peak at δ 177.0 and appearance of new peaks at δ 201.3 and 172.0 in ^{13}C NMR and at δ 1095 in ^{77}Se NMR.[11,12] These results do support the formation of *O*-benzoyl selenoester (**33**) by a process involving O-aroylation of **32** with benzoyl chloride. When the reaction mixture was treated with water, these peaks disappeared, and the formation of benzoic acid (**34**) was observed. The result would imply that aroylation of HSe^-, O-aroylation of **32** (**32** → **33**), and hydrolysis (**33** → **34**) took place in sequence, as outline in Scheme II.

In a similar manner, the reaction of amine salt of hydrogen selenide with an acyl halide (stearoyl chloride, 2 equiv) was also monitored by ^{13}C NMR. At the initial stage, peaks appeared at δ 191.6 and 178.1, but both peaks disappeared ultimately and a new peak at δ 198.2 increased, which corresponds to carbonyl carbon of bis(stearoyl) selenide (**11**). These results are consistent with the hypothesis that O-acylation product (**35**) was formed at the initial stage, and then isomerization took place to give the Se-acylation product (**11**) (Scheme III). The difference of the product in the acylation between aroylation may be due to the difference of stability between aliphatic and aromatic selenocarboxylate (**33** and **35**). O-Acylated product **35** is assumed to be less stable owing to the lack of conjugation between the aromatic ring and the selenocarbonyl group observed in aromatic one (**33**).

Next, the synthesis of bis(acyl) diselenides was examined with a similar procedure as described in the synthesis of dialkyl diselenides. However, the use of stoichiometric amount of water is less favorable for the generation of HSe_2^-, so a more practical method was designed.[13] Thus, the synthesis of bis(acyl) diselenides was examined by the monoacylation of HSe^- to selenocarboxylates, followed by oxidation with atmospheric oxygen.[14] This procedure successfully produced bis(acyl) or bis(aroyl) diselenides in good yields (Table IV). Bis(aroyl) diselenides bearing heteroaromatic rings were also synthesized without affecting these rings (runs 3 and 4).

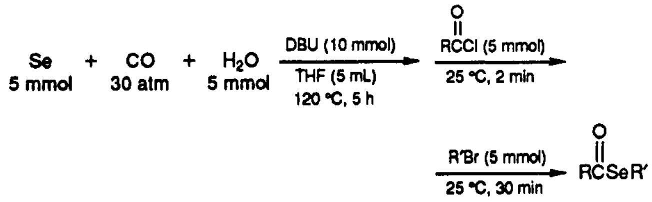
Table IV. Synthesis of Bis(acyl) Diselenides[a]

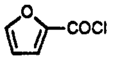
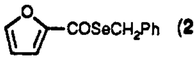
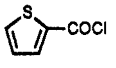
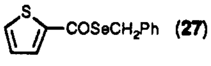


run	acyl chloride	diselenide	yield,[b] %
1		 (13)	84
2		 (14)	91
3		 (15)	93
4		 (16)	81
5	*n*-$C_{17}H_{35}COCl$	(*n*-$C_{17}H_{35}COSe)_2$ (**17**)	87
6	*n*-C_4H_9COCl	(*n*-$C_4H_9COSe)_2$ (**18**)	86
7	*s*-C_4H_9COCl	(*s*-$C_4H_9COSe)_2$ (**19**)	84
8	*t*-C_4H_9COCl	(*t*-$C_4H_9COSe)_2$ (**20**)	76

[a] All reactions were performed on a 5-mmol scale according to the procedure described in the Experimental Section. [b] Isolated yield.

Table V. Synthesis of *Se*-Alkyl Selenocarboxylates[a]



run	RCOCl	R′X	RCOSeR′	yield,[b] %
1	PhCOCl	CH_3I	$PhCOSeCH_3$ (**21**)	96
2	PhCOCl	*n*-C_4H_9Br	$PhCOSeC_4H_9$-*n* (**22**)	79
3	PhCOCl	*s*-C_4H_9Br	$PhCOSeC_4H_9$-*s* (**23**)	24
4	PhCOCl	*n*-$C_6H_{13}Br$	$PhCOSeC_6H_{13}$-*n* (**24**)	82
5	PhCOCl	$PhCH_2Br$	$PhCOSeCH_2Ph$ (**25**)	93
6		$PhCH_2Br$		80
7		$PhCH_2Br$		73
8	*n*-C_4H_9COCl	$PhCH_2Br$	*n*-$C_4H_9COSeCH_2Ph$ (**28**)	91
9	*s*-C_4H_9COCl	$PhCH_2Br$	*s*-$C_4H_9COSeCH_2Ph$ (**29**)	85
10	*t*-C_4H_9COCl	$PhCH_2Br$	*t*-$C_4H_9COSeCH_2Ph$ (**30**)	70
11	*n*-$C_{17}H_{35}COCl$	$PhCH_2Br$	*n*-$C_{17}H_{35}COSeCH_2Ph$ (**31**)	87

[a] All reactions were performed on a 5-mmol scale according to the procedure described in the Experimental Section. [b] Isolated yield.

(iii) Synthesis of *Se*-Alkyl Selenocarboxylates. During the investigation of the synthesis of bis(aroyl) selenides, tertiary amine salt of selenocarboxylates was successfully trapped with methyl iodide to give *Se*-methyl benzeneselenoate (**21**). Accordingly, alkylation with several alkyl halides provided the corresponding *Se*-alkyl selenocarboxylates in good yields.[15] The typical results are

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[9] Jensen et al. reported that the reaction of benzoyl chloride with hydrogen selenide in pyridine led to the formation of selenobenzoic acid as the primary product.[8a]

[10] Piperidinium selenobenzoate was previously prepared by the reaction of piperidine with bis(benzoyl) diselenide, see ref 7b.

[11] The spectrum of bis(benzoyl) diselenide showed peaks at δ 187.3 (C=O) in ^{13}C NMR and δ 614.7 (C(=O)Se) in ^{77}Se NMR.

[12] ^{77}Se NMR spectra of selenocarbonyl group of selenoester (PhC(=Se)OEt) was reported to appear at δ 915. See: Cullen, E. R.; Guziec, F. S., Jr.; Murphy, C. J.; Wong, T. C.; Andersen, K. K. *J. Am. Chem. Soc.* **1981**, *103*, 7055.

[13] Bis(benzoyl) diselenide was formed in poor yield (≤10%), probably due to inefficiency of generation of $HSeSe^-$ under the conditions using stoichiometric amount of water.

[14] Coexistance of a catalytic amount of iodide was efficient for air oxidation of selenocarboxylic acids (or $RCOSe^-$), see ref 7a.

[15] Several synthetic methods of *Se*-alkyl selenocarboxylates have been developed.[16] One of the most straightforward methods is the alkylation of selenocarboxylates. However, known examples of *Se*-alkyl selenocarboxylates synthesized along this strategy have been limited to a few cases,[17] because of the difficulty of the preparation of selenocarboxylates.

[16] (a) Bates, G. S.; Diakur, J.; Masamune, S. *Tetrahedron Lett.* **1976**, 4423. (b) Masamune, S.; Hayase, Y.; Schilling, W.; Chan, W. K.; Bates, G. S. *J. Am. Chem. Soc.* **1977**, *99*, 6756. (c) Grieco, P. A.; Yokoyama, Y.; Williams, E. *J. Org. Chem.* **1978**, *43*, 1283. (d) Kozikowski, A. P.; Ames, A. *J. Org. Chem.* **1978**, *43*, 2735. (e) Kato, S.; Murai, T.; Ishida, M. *Org. Prep. Proc. Int.* **1986**, *18*, 369 and references therein.

summarized in Table V. A variety of acyl or aroyl chlorides can be used as the substrates. However, the bulkiness of the alkyl halides influenced the yields of the products (run 3).

In conclusion, the results described in this paper indicate that carbon monoxide and water can selectively reduce elemental selenium to selenoate anion (HSe^- and HSe_2^-). A wide range of diorganyl selenides and diselenides were synthesized successfully by employing this reaction system.

Experimental Section

Materials. Metallic selenium (99%) from Wako Chemical Co. and carbon monoxide (99.9%) from Seitetsu Chemical Co. were used as purchased. Tertiary amines (triethylamine, *N*-methylpyrrolidine, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)), tetrahydrofuran (THF), acetonitrile, alkyl halides, benzoyl chloride, and trimethylacetyl chloride were all purchased from commercial sources and purified by distillation. The other acid chlorides were prepared by the reaction of appropriate aromatic and aliphatic acids with thionyl chloride.

Instruments. IR spectra were recorded on Shimadzu Model IR 400 or JASCO A-202, and ^1H NMR spectra were measured by Hitachi R-24B or JEOL JNM-PS-100 with Me_4Si as an internal standard. ^{13}C NMR spectra were obtained on JEOL JNM-GXS-400 with Me_4Si as an internal standard. ^{77}Se NMR spectra were recorded on JEOL JNM-PS-270 with Me_2Se as an internal standard. Analytical gas chromatograph (GLC) were carried out on Shimadzu GC-3BF equipped with a flame ionization detector using a 1.5 m × 3 mm stainless steel column packed with 5% SE-30 on 60–80-mesh Chromosorb W. Melting points were determined on Yanagimoto micro melting point apparatus and uncorrected. Mass spectra were recorded on Hitachi RMU-6A or JEOL JMS-QH-100. Elemental analyses were performed on a Yanagimoto CHN-Corder MT-2. All the products were characterized by comparison of their spectral data with those of authentic samples or by spectral and elemental analyses.

General Procedure for the Synthesis of Dialkyl Selenides. In a 50-mL stainless steel autoclave were placed selenium (0.4 g, 5 mmol), water (0.27 mL, 15 mmol), DBU (2.3 mL, 15 mmol), acetonitrile (5 mL), and a magnetic stirring bar. The apparatus was flushed three times with carbon monoxide and charged at 5 atm. The mixture was heated in an oil bath maintained at 80 °C with magnetic stirring for 1 h. After the reaction was complete, the autoclave was cooled and the remaining carbon monoxide was purged. Alkyl halide (25 mmol) was added to the reaction mixture under nitrogen atmosphere, and the solution was heated at 80 °C for additional 1 h. The reaction mixture was poured into a solution of *n*-hexane (50 mL)/water (50 mL), and the aqueous layer was extracted three times with *n*-hexane (50 mL). The combined extracts were analyzed by GLC using the internal standard method. The organic layer was dried over $MgSO_4$. Removal of the solvent under reduced pressure afforded a pale yellow oil or crystals, which by distillation (or recrystallization) gave the corresponding dialkyl selenides.

Diisobutyl selenide (2): bp 63–65 °C (13 Torr); ^1H NMR (CCl_4) δ 0.97 (d, $J = 7$ Hz, 12 H), 1.32–2.02 (m, 2 H), 2.37 (d, $J = 7$ Hz, 4 H); IR (neat) 1940, 1455, 1380, 1360 cm^{-1}; mass spectrum, *m*/*e* 194 (M^+, ^{80}Se). Anal. Calcd for $C_8H_{18}Se$: C, 49.74; H, 9.39. Found: C, 49,77; H, 9.45.

Dibenzyl Selenide (5). The reaction and workup were carried out in the same manner as described in the general procedure. Purification by recrystallization from *n*-pentane afforded dibenzyl selenide as yellow crystals.

General Procedure for the Synthesis of Dialkyl Diselenides. Method A. A stirred mixture of selenium (5 mmol), water (15 mmol), *N*-methylpyrrolidine (1.3 mL, 12 mmol), and CH_3CN (5 mL) was heated at 80 °C for 1 h under the pressure of CO (5 atm; initial pressure at 25 °C). After the reaction was complete, the autoclave was cooled and the remaining gas purged. Alkyl halide (17 mmol) was added to the reaction mixture under nitrogen atmosphere, and then the solution was heated at 80 °C for 1 h. The subsequent workup was carried out as described above. Results are listed in method A in Table III.

Diisobutyl diselenide (7): bp 86–88 °C (1.5 Torr); ^1H NMR (CCl_4) δ 1.01 (d, $J = 6$ Hz, 12 H), 1.43–2.32 (m, 2 H), 2.85 (d, $J = 6.5$ Hz, 4 H); IR (neat) 2940, 1460, 1380 cm^{-1}; mass spectrum, *m*/*e* 274 (M^+, ^{80}Se). Anal. Calcd for $C_8H_{18}Se_2$: C, 35.31; H, 6.67. Found: C, 35.28; H, 6.80.

Di-*sec*-butyl diselenide (8): bp 79–80 °C (4 Torr); ^1H NMR (CCl_4) δ 0.99 (t, $J = 6.5$ Hz, 6 H), 1.44 (d, $J = 6.5$ Hz, 6 H), 1.35–2.16 (m, 4 H), 3.00 (sextet, $J = 6$ Hz, 2 H); IR (neat) 2925, 1465, 1370 cm^{-1}; mass spectrum, *m*/*e* 274 (M^+, ^{80}Se). Anal. Calcd for $C_8H_{18}Se_2$: C, 35.31; H, 6.67. Found: C, 35.16; H, 6.92.

Method B. In a 50-mL stainless steel autoclave were placed selenium (5 mmol), water (15 mmol), DBU (10 mmol), CH_3CN (5 mL), and a magnetic stirring bar. The autoclave was charged with carbon monoxide to 5 atm at 25 °C and then heated with stirring in an oil bath maintained at 80 °C for 1 h. After the reaction, autoclave was cooled and carbon monoxide was purged. Selenium (5 mmol) was added to the reaction mixture under nitrogen atmosphere, and the mixture was stirred at 80 °C for 1 h. After the alkyl halide (20 mmol) was added, the mixture was stirred for an additional 1 h at 80 °C. The reaction mixture was worked up by the same procedure as method A. The results are given in Table III (method B).

Dibenzyl Diselenide (10). Amine salt of hydrogen diselenide was prepared by the method B. After the reaction was complete, benzyl bromide (20 mmol) was added, and the reaction mixture was heated at 80 °C for 1 h. Workup as previously described and recrystallization from *n*-hexane afforded dibenzyl diselenide as yellow crystals.

Synthesis of Bis(stearoyl) Selenide (11). A mixture of selenium (5 mmol), water (5 mmol), DBU (10 mmol), and THF (5 mL) was stirred at 120 °C for 5 h under 30 atm of carbon monoxide. After the reaction was complete, the autoclave was cooled and the remaining gas was purged. Stearoyl chloride (10 mmol) was added to the reaction mixture. After the addition was complete, the reaction mixture was stirred for 1 h. The residue was dissolved in benzene (50 mL), and the solution was washed with water. The organic layer was dried over $MgSO_4$, and evaporation of the solvent left gray crystals. Recrystallization from benzene/ether gave the corresponding bis(stearoyl) selenide.

Bis(valeryl) Selenide (12). The reaction was carried out in the same manner as described in the synthesis of bis(stearoyl) selenide. After the reaction was complete, extraction of the product with diethyl ether (30 mL × 3), followed by column chromatography on silica gel gave bis(valeryl) selenide as yellow oil: ^1H NMR (CCl_4) δ 0.92 (t, $J = 6$ Hz, 6 H), 1.10–1.90 (m, 12 H), 2.77 (t, $J = 7$ Hz, 4 H); IR (neat) 1785, 1718 cm^{-1}; mass spectrum, *m*/*e* 250 (M^+, ^{80}Se). Anal. Calcd for $C_{10}H_{18}O_2Se$: C, 48.19; H, 7.28. Found: C, 48.47; H, 7.24.

General Procedure for the Synthesis of Bis(aroyl) Diselenides. In a 50-mL stainless steel autoclave were placed selenium (5 mmol), water (5 mmol), DBU (5 mmol), THF (5 mL), and a magnetic stirring bar. The apparatus was flushed three times with carbon monoxide and charged at 30 atm. The mixture was heated in an oil bath maintained at 120 °C with magnetic stirring for 5 h. After the reaction was complete, the autoclave was cooled and the remaining gas was purged. Aroyl chloride (5 mmol) and a solution of iodide (0.06 g) in 5 mL of THF were added to the reaction mixture. After the additional was complete, the reaction mixture was stirred for an additional 4 h. The residue was dissolved in benzene (50 mL), and the solution was washed with water. The organic layer was dried over $MgSO_4$. Evaporation of the solvent left gray crystals, which were recrystallized from benzene/ether to give the corresponding bis(aroyl) diselenide.

Bis(2-furoyl) diselenide (15): mp 109–110.5 °C; ^1H NMR ($CDCl_3$) δ 6.44 (dd, $J = 2, 4$ Hz, 2 H), 7.04 (d, $J =$ Hz, 2 H), 7.49 (d, $J =$ Hz, 2 H); IR (KBr) 1692, 800, 760 cm^{-1}; mass spectrum, *m*/*e* 350 (M^+, ^{80}Se). Anal. Calcd for $C_{10}H_6O_4Se_2$: C, 34.50; H, 1.73. Found: C, 34.76; H, 1.83.

Bis(2-thienyl) diselenide (16): mp 115.5–116 °C; ^1H NMR ($CDCl_3$) δ 6.99 (t, $J = 4$ Hz, 2 H), 7.54 (d, $J = 4$ Hz, 2 H), 7.70 (d, $J = 4$ Hz, 2 H); IR (KBr) 1690, 770 cm^{-1}; mass spectrum, *m*/*e* 382 (M^+, ^{80}Se). Anal. Calcd for $C_{10}H_6O_2S_2Se_2$: C, 31.59; H, 1.59 %. Found: C, 31.87; H, 1.73 %.

Bis(valeryl) Diselenide (18). The reaction was carried out in the same manner as described in the general procedure of

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(17) (a) Ishihara, H.; Hirabayashi, Y. *Chem. Lett.* **1976**, 203. (b) Ishihara, H.; Hirabayashi, Y. *Chem. Lett.* **1978**, *1007*, and refs 7b and 8a.

bis(aroyl) diselenide. After the reaction was complete, extraction of the product with diethyl ether (30 mL × 3), followed by column chromatography on silica gel, gave bis(valeryl) diselenide as yellow oil; ^{1}H NMR (CCl_4) δ 0.95 (t, J = 8 Hz, 6 H), 1.20–1.85 (m, 12 H), 2.80 (t, J = 8 Hz, 4 H); IR (neat) 1730 cm^{-1}; mass spectrum, m/e 330 (M$^+$, ^{80}Se). Anal. Calcd of $C_{10}H_{18}O_2Se_2$: C, 36.60; H, 5.33. Found: C, 36.24; H, 5.27.

Bis(2-methylbutyryl) Diselenide (19). The reaction was carried out in the same manner as the synthesis of bis(valeryl) diselenide: ^{1}H NMR (CCl_4) δ 0.95 (t, J = 8 Hz, 6 H), 1.18 (d, J = 7 Hz, 6 H), 1.31–1.91 (m, 4 H), 2.82 (sextet, J = 7 Hz, 2 H); IR (neat) 1730 cm^{-1}; exact mass, m/e 329.9634 (theory 329.9637).

Bis(2,2-dimethylpropionyl) Diselenide (20). The reaction was carried out in the same manner as the synthesis of bis(valeryl) diselenide: ^{1}H NMR (CCl_4) δ 1.28 (s, 18 H); IR (neat) 1782, 1731 cm^{-1}; exact mass, m/e 329.9639 (theory 329.9637).

NMR Experience for the Determination of the Reaction Path on the Synthesis of Bis(benzoyl) Selenide. The preparation of tertiary amine salt of hydrogen selenide was carried out in the same manner as described in the synthesis of bis(acyl) selenides. After the reaction was complete, 1 equiv of benzoyl chloride was added to the reaction mixture under a nitrogen atmosphere, and the solvent was evaporated in vacuo. The resulting mixture (0.2 mL) was placed in a 5-mm diameter NMR sample tube, and ^{13}C NMR was measured by using benzene-d_6 (0.8 mL) as a solvent: ^{13}C NMR (benzene-d_6) δ 177.0 (assigned to C=O). After the measurement, another 1 equiv of benzoyl chloride was added dropwise by syringe, and then ^{13}C and ^{77}Se NMR measurements were performed: ^{13}C NMR (benzene-d_6) δ 201.2 (assigned to C=Se) and 172.2 (C=O); ^{77}Se NMR δ 1095 (C=Se).

Similar NMR Experiment on the Synthesis of Bis(stearoyl) Selenide. NMR experiment was carried out in a similar manner as described above. ^{13}C NMR spectra, obtained just immediately after 2 equiv of stearoyl chloride was added, is as follows: ^{13}C NMR δ 191.6 (assigned to C=Se) and δ 178.1 (C=O). Isomerization to bis(stearoyl) selenide took place within an hour, and the ^{13}C NMR spectral data is as follows: ^{13}C NMR δ 198.2 (C=O).

General Procedure for the Synthesis of *Se*-Alkyl Selenocarboxylates. In a 50-mL stainless steel autoclave were placed selenium (5 mmol), water (5 mmol), DBU (10 mmol), and THF (5 mL), and the mixture was heated with magnetic stirring under the pressure of carbon monoxide (30 atm; initial pressure at 25 °C) at 120 °C for 5 h. After the reaction, carbon monoxide was purged in a well-ventilated hood. Acid chloride (5 mmol) in THF (15 mL) was added to the resulting solution at 0 °C under nitrogen, followed immediate alkylation with alkyl halide (5 mmol) in THF (5 mL) at 0 °C. The resulting mixture was extracted with diethyl ether (30 mL × 2) and benzene (30 mL × 1) and dried over $MgSO_4$. Removal of the solvent in vacuo, followed by purification by column chromatography on silica gel, afforded the corresponding *Se*-alkyl selenocarboxylates.

***Se*-Methyl benzeneselenoate (21):** ^{1}H NMR (CCl_4) δ 2.30 (s, 3 H), 7.12–7.46 (m, 3 H), 7.68 (dd, J = 2, 7 Hz, 2 H), IR (neat) 1665 cm^{-1}; mass spectrum, m/e 200 (M$^+$, ^{80}Se). Anal. Calcd for C_8H_8OSe: C, 48.26; H, 4.05. Found: C, 48.51; H, 4.02.

***Se*-Butyl benzeneselenoate (22):** ^{1}H NMR (CCl_4) δ 0.96 (t, J = 7 Hz, 3 H), 1.25–1.88 (c, 4 H), 3.00 (t, J = 6 Hz, 2 H), 7.12–7.38 (m, 3 H), 7.70 (dd, J = 2, 8 Hz, 2 H); IR (neat) 1673 cm^{-1}; mass spectrum, m/e 242 (M$^+$, ^{80}Se). Anal. Calcd for $C_{11}H_{14}OSe$: C, 54.78; H, 5.85. Found: C, 54.82; H, 5.61.

***Se*-*sec*-Butyl benzeneselenoate (23):** ^{1}H NMR (CCl_4) δ 1.00 (t, J = 8 Hz, 3 H), 1.46 (d, J = 8 Hz, 3 H), 1.60–1.90 (m, 2 H), 3.64 (sextet, J = 8 Hz, 1 H), 7.12–7.38 (m, 3 H), 7.71 (dd, J = 2, 8 Hz, 2 H); IR (neat) 1675 cm^{-1}; mass spectrum, m/e 242 (M$^+$, ^{80}Se). Anal. Calcd for $C_{11}H_{14}OSe$: C, 54.78; H, 5.85. Found: C, 54.97; H, 5.93.

***Se*-Hexyl benzeneselenoate (24):** ^{1}H NMR (CCl_4) δ 0.88 (t, J = 6 Hz, 3 H), 1.08–1.88 (m, 8 H), 3.03 (t, J = 7 Hz, 2 H), 7.16–7.52 (m, 3 H), 7.80 (dd, J = 2, 8 Hz, 2 H); IR (neat) 1662 cm^{-1}; mass spectrum, m/e 270 (M$^+$, ^{80}Se). Anal. Calcd for $C_{13}H_{18}OSe$: C, 59.33; H, 6.89. Found: C, 59.62; H, 6.74.

***Se*-Benzyl benzeneselenoate (25):** ^{1}H NMR (CCl_4) δ, 4.18 (s, 2 H), 6.94–7.36 (m, 8 H), 7.72 (dd, J = 2, 8 Hz, 2 H); IR (neat) 1675 cm^{-1}; mass spectrum, m/e 276 (M$^+$, ^{80}Se). Anal. Calcd for $C_{14}H_{12}OSe$: C, 61.10; H, 4.39. Found: C, 60.86; H, 4.50.

***Se*-Benzyl 2-furancarboselenoate (26):** mp 53.5–55.0 °C; ^{1}H NMR (CCl_4) δ 4.11 (s, 2 H), 6.30 (dd, J = 2, 4 Hz, 1 H), 6.80–7.16 (c, 6 H), 7.30 (d, J = 2 Hz, 1 H); IR (KBr) 1670 cm^{-1}; mass spectrum, m/e 266 (M$^+$, ^{80}Se). Anal. Calcd for $C_{12}H_{10}O_2Se$: C, 45.30; H, 3.80. Found: C, 45.68; H, 3.74.

***Se*-Benzyl 2-thiophenecarboselenoate (27):** mp 59.5–61.0 °C; ^{1}H NMR (CCl_4) δ 4.18 (s, 2 H), 6.82–7.20 (c, 6 H), 7.37 (d, J = 6 Hz, 1 H), 7.50 (d, J = 4 Hz, 3 H); IR (KBr) 1679 cm^{-1}; mass spectrum, m/e 282 (M$^+$, ^{80}Se). Anal. Calcd for $C_{12}H_{10}OSSe$: C, 51.25; H, 3.58. Found: C, 50.91; H, 3.64.

***Se*-Benzyl pentaneselenoate (28):** ^{1}H NMR (CCl_4) δ 0.85 (t, J = 7 Hz, 3 H), 1.10–1.65 (m, 4 H), 2.50 (t, J = 8 Hz, 2 H), 3.95 (s, 2 H), 7.05 (s, 5 H); IR (neat) 1700 cm^{-1}; mass spectrum, m/e 256 (M$^+$, ^{80}Se). Anal. Calcd for $C_{12}H_{16}OSe$: C, 56.47; H, 6.32. Found: C, 56.82; H, 6.25.

***Se*-Benzyl 2-methylbutaneselenoate (29):** ^{1}H NMR (CCl_4) δ 0.91 (t, J = 7 Hz, 3 H), 1.14 (d, J = 7 Hz, 3 H), 1.20–1.92 (m, 2 H), 2.52 (sextet, J = 7 Hz, 1 H), 4.00 (s, 2 H), 7.07 (s, 5 H); IR (neat) 1705 cm^{-1}; mass spectrum, m/e 256 (M$^+$, ^{80}Se). Anal. Calcd for $C_{12}H_{16}OSe$: C, 56.47; H, 6.32. Found: C, 56.40, H, 6.48.

***Se*-Benzyl 2,2-dimethylpropaneselenoate (30):** ^{1}H NMR (CCl_4) δ 1.20 (s, 9 H), 3.94 (s, 2 H), 7.00 (s, 5 H); IR (neat) 1720, 1696 cm^{-1}; mass spectrum, m/e 256 (M$^+$, ^{80}Se). Anal. Calcd for $C_{12}H_{16}OSe$: C, 56.47; H, 6.32. Found: C, 56.81; H, 6.50.

***Se*-Benzyl octadecaneselenoate (31):** mp 53.0–54.5 °C, ^{1}H NMR (CCl_4) δ 0.83 (t, J = 7 Hz, 3 H), 1.30 (s, 2 H), 1.50–1.75 (m, 2 H), 2.49 (t, J = 8 Hz, 2 H), 3.97 (s, 2 H), 7.04 (s, 5 H); IR (KBr) 1723, 1710 cm^{-1}; mass spectrum, m/e 438 (M$^+$, ^{80}Se). Anal. Calcd for $C_{25}H_{42}OSe$: C, 68.62; H, 9.67. Found: C, 68.65; H, 9.85.

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Supplementary Material Available: Spectral data for compounds 1, 3–6, 9–11, 13–14, and 17 (2 pages). Ordering information is given on any current masthead page.