**K**Article

## Phenyl Tributylstannyl Selenide as a Promising Reagent for Introducion of the Phenylseleno Group

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A new synthetic method of organoselenium compounds has been developed. When phenyl tributylstannyl selenide (PhSeSnBu<sub>3</sub>) was allowed to react with acyl or aroyl chlorides in the presence of a catalytic amount of a palladium complex such as Pd(PPh<sub>3</sub>)<sub>4</sub>, Se-phenyl selenol esters were obtained in moderate to good yields. Similarly, the palladium complex catalyzed the reaction of PhSeSnBu<sub>3</sub> with  $\alpha$ -halo carbonyl compounds to afford the corresponding  $\alpha$ -phenyseleno carbonyl compounds in moderate yields.

## Introduction

Since Sharpless and Reich have demonstrated an effective olefin-forming method by the use of selenoxide elimination in the early 1970s,<sup>1</sup> the interest in the utility of organoselenium compounds in organic synthesis grew. In the organic chemistry by the use of organoselenium compounds as key intermediates, the organoselenium compounds are often diorganyl selenides, and much effort is being devoted to accomplish the synthesis of these compounds.<sup>2</sup> However, many synthetic methods sometimes suffer from the improper handling of selenium reagents used as selenium sources because of their instability against air and moisture and basic or acidic reaction conditions. Thus, the development of new synthetic methods using stable selenium reagents under mild conditions would have significant synthetic value.

Transition metal complex catalyzed reactions of aryl halides with organoheteroatom compounds having M-M' (M and M' = heteroatom) bonds are now widely used for the synthesis of various heteroatom-containing compounds;<sup>3</sup> however, similar reactions of aryl halides with organoselenium compounds containing a selenium—heteroatom bond have not been reported. Our and Beletskaya's groups have recently shown that the palladium complex catalyzed the coupling reaction of phenyl tributylstannyl selenide (PhSeSnBu<sub>3</sub>) (1), which is stable against air and moisture, with aryl halides giving the corresponding diaryl selenides in moderate to good yields.<sup>4</sup> In the course of our study on the utilization of phenyl tributylstannyl selenide, in organic reactions,<sup>5-7</sup>

we found that Se-phenyl selenol esters and  $\alpha$ -phenylseleno carbonyl compounds were synthesized by the palladium complex-catalyzed reaction of **1** with acid chlo-

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rides and  $\alpha$ -halo carbonyl compounds in moderate to good vields.

## **Results and Discussion**

(1) Synthesis of Se-Phenyl Selenol Esters. The development of a convenient and efficient method for the synthesis of Se-phenyl selenol esters has attracted considerable attention<sup>9</sup> because they are useful transfer reagents for acyl or aroyl groups onto the various organic compounds.<sup>10–12</sup> Then, the synthesis of Se-phenyl selenol esters by reaction of phenyl tributylstannyl selenide (1) with benzoyl chloride (2a) in the presence of a catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub> was examined. When 1 was allowed to react with 2a in the presence of a catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub> at 25 °C for 6 h, Se-phenyl seleno benzoate (3a) was formed in 97% yield (entry 1, Table 1).<sup>17</sup> The results of the synthesis of various Se-phenyl selenol esters by the palladium-catalyzed coupling of **1** with aroyl or acyl chlorides are shown in Table 1. The treatment of **1** with p-methyl-, p-methoxy-, p-chloro-, p-nitro-, and p-cyanobenzoyl chloride under reaction conditions similar to those for 2a afforded the corresponding Se-aryl selenol esters in 71-91% yields (entries 2-6). In the reaction of 1- and 2-naphthyl acid chloride, the coupling reaction also proceeded to give selenol esters in 87 and 92% yields, respectively (entries 7 and 8). Similarly, the coupling reaction of 1 with acyl chlorides having a linear alkyl chain or benzylic group was successfully occurred, and Se-aryl selenol esters were obtained in 92 and 85% yield (entries 9 and 10). However, in the case of  $\alpha$ -methyl- and  $\alpha,\alpha$ -dimethyl-substituted acyl chloride, the yields of product were slightly decreased (entries 11 and 12).

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(12) Selenol esters can also be converted to the corresponding acids,<sup>13</sup> esters,<sup>13</sup> amides,<sup>13</sup> ketones,<sup>14</sup> aldehydes,<sup>15</sup> and alkenyl selenides.<sup>16</sup> (13) (a) Kozikowsky, A. P.; Ames, A. *J. Org. Chem.* **1978**, *43*, 2735.

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(17) Beletskaya has shown the synthetic method of selenol esters by the reaction of acyl and aroyl chloride with PhSeSnBu<sub>3</sub>, which was generated in situ by the reaction of PhSeSePh with Bu<sub>3</sub>SnSnBu<sub>3</sub> under daylight conditions, in the absence of palladium catalyst. Thus, we examined the reaction of PhSeSnBu3, which was synthesized by our method (see the Experimental Section), and benzoyl chloride under the similar reaction conditions to that of Beletskaya's report; however, the yield of Se-phenyl selenobenzoate (7) was low (24%).

TABLE 1. Palladium-Catalyzed Reaction of PhSeSnBu<sub>3</sub> with Aroyl or Acyl Chlorides<sup>a</sup>

			cat. Dd	
PhSeSnBu <sub>3</sub>	+	ArCOCI	<b>F</b> u	ArCOSePh
1		(RCOCI)		(RCOSePh)
		2		3

Entry	RCOCI	Product	Yield/% <sup>b)</sup>
	x COCI	x COSePh	
1	X = H (2a)	(3a)	97
2	= CH <sub>3</sub> (2b)	(3b)	83
3	= CH <sub>3</sub> O <b>(2c)</b>	(3c)	80
4	= Cl (2d)	(3d)	91
5	= NO <sub>2</sub> (2e)	(3e)	83
6	= CN (2f)	(3f)	71
7	(2g)	COSePh (3g)	87
8	(2h)	COSePh (3h)	92
9	Cl (2i)	SePh (3i)	92
10	O (2j)	O SePh (3j)	85
11	O CI (2k)	O SePh (3k)	74
12	0 (21)	O SePh (3I)	51

<sup>a</sup> Reaction conditions: 1 (0.25 mmol), aroyl or acyl chloride (0.25 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (1 mol %) and toluene (2 mL) at 25 °C for 6 h. <sup>b</sup> GC yield.

Although a detailed study on the reaction pathway has not yet been completed, a plausible catalytic pathway was shown in Scheme 1. The first step involves the oxidative addition of the aroyl chloride to the low-valent palladium species to form an aroylpalladium chloride species (4).<sup>18,19</sup> The following ligand exchange of 4 with PhSeSnBu<sub>3</sub> generates the intermediate 5. The subsequent reductive elimination from 5 affords the coupling product and regenerate the low-valent palladium species.

<sup>(8)</sup> The bond energy of the Se–Sn bond is  $D_{298}^{0} = 98.2 \pm 3$  kcal/ mol. See: Ho, K. C. M. In Thermodynamic Data for Inorganic Sulfides, Selenides, and Tellurides; Rechhood Press: England, 1974; p 594.

<sup>(18)</sup> Tanaka disclosed that the reaction of PhSeSnMe<sub>3</sub> with Pt(PEt)<sub>3</sub> took place rapidly (<10 min) at room temperature to afford trans-Pt-(SePĥ)(SnMe₃)(PĚt₃) in 85% isolated yield. See; Han, L.-B.; Shinoda, S.; Tanaka, M. J. Am. Chem. Soc. 1997, 119, 8135.



(2) Synthesis of a-Phenylseleno Carbonyl Compounds. a-Phenylseleno carbonyl compounds were useful intermediates for the generation of the enolate anion<sup>20</sup> and  $\alpha$ -carbonyl carbon radicals<sup>21</sup> in organic synthesis, and much effort is being devoted to accomplish the synthesis of  $\alpha$ -phenylseleno carbonyl compounds.<sup>22</sup> Thus, we have examined the palladium-catalyzed reaction of PhSeSnBu<sub>3</sub> (1) with  $\alpha$ -bromocarbonyl compounds (6). When 1 was allowed to react with  $\alpha$ -bromoacetophenone (6a) in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %) at 80 °C for 6 h,  $\alpha$ -phenylseleno acetophenone (7a) was obtained in 90% yield (entry 1, Table 2). Similarly, the palladium complex catalyzed the coupling of p-methyl-, p-cyano-, pchloro-, and *p*-nitro- $\alpha$ -bromoacetophenone to give the corresponding  $\alpha$ -phenylselenoacetophenones in moderate yields (entries 2 and 4–6). For *p*-methoxy- $\alpha$ -bromoacetophenone, the yield of coupling product was low under reaction conditions similar to those for  $\alpha$ -bromoacetophenone; however, the yield of product was improved by elevating the reaction temperature (110 °C) (entry 3). In the case of  $\alpha$ -chloroacetophenone, the yield of  $\alpha$ -phenylselenoacetophenone was low (22%) (entry 7). In this coupling reaction, the yields of products were influenced by the steric effect of the  $\alpha$ -position. Although the coupling reaction of 1 with  $\alpha$ -bromopropiophenone gave  $\alpha$ -phe-

IO	CΔ	rtic	10
JO	$C_{II}$	1110	υ

**TABLE 2.** Synthesis of Various α-Phenylseleno Carbonyl Compounds<sup>a</sup>

arbonyi Compounds"							
Entry	RCOCH <sub>2</sub> Br	•	Product Yie	eld/% <sup>b)</sup>			
	x	,Br	SePh				
1	X = H	(6a)	(7a)	90			
2	= CH <sub>3</sub>	(6b)	(7b)	60			
3 <sup>c)</sup>	= OCH <sub>3</sub>	(6c)	(7c)	46			
4	= CI	(6d)	(7d)	43			
5	= NO <sub>2</sub>	(6e)	(7e)	50			
6	= CN	(6f)	(7f)	46			
7	CI	(6g)	(7a)	22			
8 <sup>c)</sup>	B	(6h)	SePh (7h)	84			
9 <sup>c)</sup>	O Br	「(6i)	SePh (7i)	22			
10	O Br	(6j)	SePh (7j)	48			
11	O Br	(6k)	0 	56			
12	O Br	(61)	O SePh (7I)	52			

<sup>&</sup>lt;sup>*a*</sup> Reaction conditions: **1** (0.25 mmol), α-bromo carbonyl compound (0.25 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %) and toluene (2 mL) at 80 °C for 6 h. <sup>*b*</sup> GC yield. <sup>*c*</sup> At 110 °C.

nylselenopropiophenone in 84% yield, in the case of  $\alpha$ -bromo- $\alpha$ -methylpropiophenone, the yield of  $\alpha$ -phenylseleno ketone was low compared with  $\alpha$ -bromopropiophenone (entries 8 and 9). An  $\alpha$ -bromo dialkyl ketone such as 2-bromo-3-pentanone as well as  $\alpha$ -bromoalkyl phenyl ketone was coupled with 1 giving 2-phenylseleno-3pentanone in 48% yield (entry 10). Similarly,  $\alpha$ -pheylseleno esters were successfully synthesized by the palladiumcatalyzed reaction of 1 with  $\alpha$ -bromo esters (entries 11 and 12).

In summary, the coupling reaction of PhSeSnBu<sub>3</sub>, which is stable against air and moisture, with acyl or aroyl chlorides in the presence of a catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub> efficiently proceeded to give the corresponding selenol esters in moderate to good yields. The palladium complex also acts as a catalyst for the coupling of PhSeSnBu<sub>3</sub> with  $\alpha$ -halo carbonyl compounds to give the corresponding  $\alpha$ -phenylseleno carbonyl compounds in moderate yields. This method has some noteworthy

<sup>(19)</sup> Rossi has reported the synthesis of (*E*)-1-alkenyl phenylsulfides by the palladium-catalyzed reaction of 1-alkenyl bromides with trialkylstannyl phenylsulfide. In this paper, they proposed that the first step of this reaction was the generation of vinylpalladium bromide species by the reaction of 1-alkenyl bromides with low-valent palladium species. See: Carpita, A.; Rossi, R.; Scamuzzi, B. *Tetrahedron Lett.* **1989**, *30*, 2699.

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features: (i) the use of stable organoselenium reagent against air and moisture; (ii) the high and moderate yield preparation method of organoselenium compounds; (iii) neutral reaction conditions; and (iv) ease of operation. A wide range of organoselenium compounds were synthesized successfully by employing this palladium-catalyzed reaction system.

## **Experimental Section**

**General Procedure.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on 400 and 99.5 MHz spectrometers using CDCl<sub>3</sub> as solvent with tetramethylsilane as the internal standard. IR spectra were obtained on an FT-IR spectrophotometer. Mass spectra were measured on GC–MS. Gass chromatography (GC) was carried out on a spectrometer flame-ionizing detector using a capillary column.  $\alpha$ -Bromo carbonyl compounds, palladium complexes, and tributylstannyl chloride were commercially available and used without purification. Aroyl and acyl chlorides and solvents were commercially available and purified by the usual methods before use. Diphenyl diselenide was synthesized by the literature procedure. <sup>26</sup>

**Preparation of Phenyl Tributylstannyl Selenide.** Bu<sub>3</sub>SnCl (5.208 g, 16 mmol) was added to the PhSeNa (16 mmol), which was generated in situ by the literature method,<sup>27</sup> in EtOH/THF (2 mL/30 mL) solution at 0 °C and stirred at 25 °C for 3 h. After the reaction was complete, H<sub>2</sub>O was added to the resulting solution and extracted with diisopropyl ether (×5). The combined organic layer was washed with brine and dried over MgSO<sub>4</sub>. The organic solvent was removed under reduced pressure. The residual oil was purified by distillation with Kugelrohr under reduced pressure (1 mmHg) to yield PhSeSnBu<sub>3</sub> (1) (72%): <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS)  $\delta$  0.87 (t, *J* = 7.6 Hz, 9H), 1.11 (t, *J* = 7.6 Hz, 6H), 1.28 (sextet, *J* = 7.6 Hz, 6H), 1.50 (quintet, *J* = 7.6 Hz, 6H), 7.12–7.19 (m, 3H), 7.52–7.55 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>/TMS)  $\delta$  13.79, 14.24, 27.17, 29.00, 126.40, 128.77, 136.81, 136.85

General Procedure for the Pd(PPh<sub>3</sub>)<sub>4</sub>-Catalyzed Synthesis of Se-Phenyl Selenol Esters by the Reaction of PhSeSnBu<sub>3</sub> with Aroyl or Acyl Chlorides. Aroyl or acyl chlorides (0.25 mmol) and PhSeSnBu<sub>3</sub> (112 mg, 0.25 mmol) were added to a toluene (2 mL) solution of Pd(PPh<sub>3</sub>)<sub>4</sub> (3 mg, 0.0025 mmol), and the reaction mixture was stirred at 25 °C for 6 h under nitrogen atmosphere. After the reaction was complete, H<sub>2</sub>O was added to the resulting solution and extracted with diisopropyl ether (×5). The combined organic layer was washed with brine and aq KF and dried over MgSO<sub>4</sub>. The organic solvent was removed under reduced pressure. Purification by column chromatography (C<sub>6</sub>H<sub>14</sub>/AcOEt = 50/1) on silica gel gave the corresponding Se-phenyl selenol esters.

General Procedure for the Pd(PPh<sub>3</sub>)<sub>4</sub>-Catalyzed Reaction of PhSeSnBu<sub>3</sub> with  $\alpha$ -Bromo Carbonyl Compound.  $\alpha$ -Bromo carbonyl compounds (0.25 mmol) and PhSeSnBu<sub>3</sub> (112 mg, 0.25 mmol) were added to a toluene (2 mL) solution of Pd(PPh<sub>3</sub>)<sub>4</sub> (15 mg, 0.0125 mmol), and the reaction mixture was stirred at 80 °C for 6 h under nitrogen atmosphere. After the reaction was complete, H<sub>2</sub>O was added to the resulting solution and extracted with diisopropyl ether (×5). The combined organic layer was washed with brine and aq KF and dried over MgSO<sub>4</sub>. The organic solvent was removed under reduced pressure. Purification by column chromatography (C<sub>6</sub>H<sub>14</sub>/AcOEt = 6/1) on silica gel gave the corresponding  $\alpha$ -phenylseleno carbonyl compounds.

**Supporting Information Available:** Copies of spectra (<sup>1</sup>H, <sup>13</sup>C and IR) for all coupling products. This material is available free of charge via the Internet at http://pubs.acs.org.

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