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Utilization of Phenyl Trialkylstannyl Selenide as a Promising Reagent for Introduction of the Phenylseleno Group

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Abstract: New synthetic methods of organoselenium compounds by the use of phenyl tributylstannyl selenide ($PhSeSnBu_3$) (**1**), which is a stable selenium reagent in air and moisture, as a phenylselenated reagent have been developed. In the presence of palladium complex catalyst, the reaction of **1** with organohalogen compounds took place efficiently to give the corresponding organoselenium compounds in moderate to good yields. Furthermore, it was found that Lewis acid assisted the reaction of **1** with oxygen-containing compounds giving the corresponding organoselenium compounds.

Keywords: Phenyl tributylstannyl selenide, palladium catalyst, organoselenium compound, Lewis acid, aryl halide, aroyl halide, carbon monoxide, α-bromo ketone, acetal, epoxide.

1. INTRODUCTION

Since Sharpless [1] and Reich [2] have shown that an effective olefin-forming method by the use of selenoxide elimination in the early 1970s, the interest in the use of organoselenium compounds in organic synthesis grew [3]. In the organic chemistry of selenium, the key intermediates are often diorganyl selenides, and much effort is being devoted to accomplish the synthesis of these compounds.

There have been a considerable interest in the clarification of the specific chemical properties of organoselenium compounds possessing selenium-metal bonds such as Se-Al, Se-B, Se-Si and Se-Sn and the development of the synthetic reactions based on the characteristic features of these compounds. Although the utility of organoselenium compounds possessed Se-Al, Se-B and Se-Si bonds is established in organic synthesis, the synthetic application of organoselenium compounds having Se-Sn bond [4], which are stable compounds in air and moisture, still remain unexplored due to the lack of method for activation of the selenium-tin bonds [5]. This short review deals with new methods for introducing of phenylseleno group into organic molecules by the use of phenyl tributylstannyl selenide.

2. TRANSITION METAL-CATALYZED REACTION OF PHENYL TRIBUTYLSTANNYL SELENIDE WITH ORGANOHALOGEN COMPOUNDS

Although transition metal complex-catalyzed reaction of organoheteroatom compounds having M-M' (M and M' = heteroatom) bonds with aryl halides are now widely used for the synthesis of various heteroatom-containing compounds, similar reaction of organoselenium compounds with organohalogen compounds has remained largely unexpected. This might be partly due to the widespread prejudice that chalcogen compounds including selenium often bind strongly to the metal catalysts, thus poisoning them and making the catalytic reaction ineffectively. We have found that the palladium complex catalyzed the coupling reaction of phenyl tributylstannyl selenide ($PhSeSnBu_3$) with organohalogen compounds giving the corresponding organoselenium compounds in moderate to good yields [13].

2-1. Reaction of Phenyl Tributylstannyl Selenide with Aryl and Alkyl Halides [14]

Reaction of phenyl tributylstannyl selenide (**1**) with iodobenzene (**2**) in the presence of a catalytic amount of $Pd(PPh_3)_4$ in toluene solvent took place efficiently, giving the diphenyl selenide (**3**) in 75 % yield (Scheme **1**).

Although the reaction of **1** with **2** proceeded, even upon with DMF, CH_3CN, THF and $CHCl_3$ instead of toluene as the solvent, the yields of **3** were slightly decreased (DMF: 60%, CH_3CN: 35 %, THF: 42 %, $CHCl_3$: 7 %). The other palladium complexes such as $Pd(Ph_2PCH_2CH_2PPh_2)$, $PdCl_2(CH_3CN)_2$, $PdCl_2(PhCN)_2$, $PdCl_2(PPh_3)_2$, $PdCl_2$, $Pd(OAc)_2$ and $PdCl_2(1,5\text{-}C_8H_{12})_2$ did not exhibit catalytic activity. When **1** was reacted with bromo- and chlorobenzene under the same reaction conditions as that of **2**, the yield of diphenyl selenide (**3**) was slightly low; however, the yields of product were improved by elevating the reaction temperature and the increasing the amounts of palladium catalyst and aryl halides. This method could be applied to a variety of aryl iodides (Table **1**). The coupling of **1** with 1-iodo-4-methyl- and 1-iodo-4-methoxybenzene was successfully undertaken by a extending the reaction time. In this reaction, the $Pd(PPh_3)_4$ also catalyzed the reaction of **1**

$$\begin{array}{ccccc} PhSeSnBu_3 & + & PhI & \xrightarrow[\text{Toluene (2 mL), 80 °C, 0.5h}]{Pd(PPh_3)_4\text{ (5 mol\%)}} & PhSePh \\ \mathbf{1} & & \mathbf{2} & & \mathbf{3} \\ \text{(0.25 mmol)} & & \text{(0.25 mmol)} & & 75\ \% \end{array}$$

Scheme 1.

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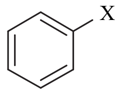
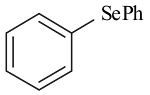
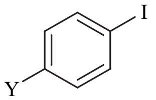
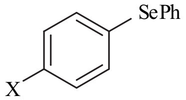
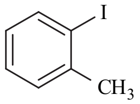
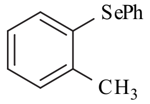
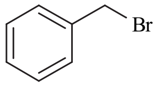
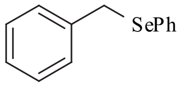
Table 1. Synthesis of Various Diorganyl Selenides[a)]

Entry	RX	Time/h	Product	Yield/%[b)]
				
1[c)]	X = Cl	8		(60)
2[d)]	X = Br	8		(79)
3	X = I	0.5		75
				
4	Y = CH_3	2		81
5	Y = OCH_3	4		88
6	Y = NO_2	0.5		70
7	Y = OH	5		50
8[e)]	Y = NH_2	5		53
9		5		47
10		8		57
11	$C_8H_{17}I$	24	$C_8H_{17}SePh$	62

[a)] Reaction conditions. $PhSeSnBu_3$ (**1**) (0.25 mmol), organic halide (0.25 mmol), $Pd(PPh_3)_4$ (5 mol%) and toluene (2 mL) at 80 °C. [b)] Isolated yield. The number in parenthesis indicates the GC yield. [c)] PhCl (2.5 mmol) and $Pd(PPh_3)_4$ (15 mmol%) at 110 °C. [d)] PhBr (0.5 mmol) and $Pd(PPh_3)_4$ (15 mol%) at 110 °C. [e)] 110 °C.

with aromatic iodides bearing hydroxyl and amino groups, which have strong coordination ability to palladium metal, giving the corresponding diaryl selenides in 50 and 53 % yields, respectively. Aliphatic halides as well as aromatic halides were reacted with **1**, and the corresponding alkyl phenyl selenides were formed in moderate yields.

To further show the usability of this palladium-catalyzed reaction as a practical method for the synthesis of diorganyl selenide, the reaction of butyl tributylstannyl selenide ($BuSeSnBu_3$) with iodobenzene was examined and found that $BuSeSnBu_3$ also acts as a promising reagent for introducing the butylseleno group to the aromatic ring, giving butyl phenyl selenide in 79 % yield (Scheme **2**). Furthermore, when bis(tributylstannyl) selenide ($Bu_3SnSeSnBu_3$) was allowed to react with 2 equiv. of iodobenzene (**2**) in the presence of $Pd(PPh_3)_4$ (10 mol%) at 80 °C for 1 h, diphenyl selenide (**3**), in which two phenyl groups were introduced onto the selenium atom, was obtained in 53 % yield (Scheme **3**).

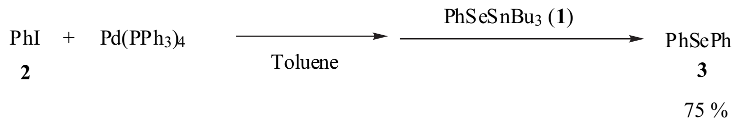
It is interesting to note that the yield of product was significantly influenced by the order of the addition of **1** and aryl iodide in this reaction. The reaction of $Pd(PPh_3)_4$ with

$$\underset{(0.25\ \text{mmol})}{\text{BuSeSnBu}_3} \quad + \quad \underset{(0.25\ \text{mmol})}{\underset{\mathbf{2}}{\text{PhI}}} \quad \xrightarrow[]{\substack{\text{Pd(PPh}_3)_4\ (10\ \text{mol\%}) \\ \text{Toluene (2 mL), 80 °C, 3h}}} \quad \underset{79\ \%}{\text{BuSePh}}$$

Scheme 2.

$$\underset{(0.25\ \text{mmol})}{\text{Bu}_3\text{SnSeSnBu}_3} \quad + \quad \underset{(0.50\ \text{mmol})}{\underset{\mathbf{2}}{\text{PhI}}} \quad \xrightarrow[]{\substack{\text{Pd(PPh}_3)_4\ (10\ \text{mol\%}) \\ \text{Toluene (2 mL), 80 °C, 1h}}} \quad \underset{53\ \%}{\underset{\mathbf{3}}{\text{PhSePh}}}$$

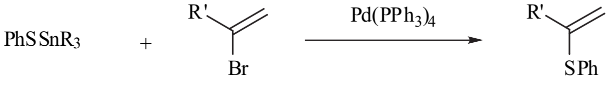
Scheme 3.



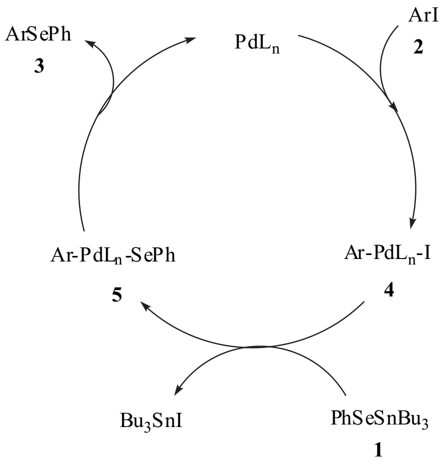
Scheme 4.

Scheme 5.

iodobenzene (**2**) in toluene solvent followed by the addition of PhSeSnBu$_3$ (**1**) results in 75 % yield of PhSePh (**3**) (Scheme **4**). In contrast, when **1** was first added to the toluene solution of Pd(PPh$_3$)$_4$, **3** was formed in only a 20 % yield (Scheme **5**). Rossi *et al.* has already reported the synthesis of 1-alkenyl phenyl sulfides by the palladium-catalyzed reaction of 1-alkenyl bromides with phenyl trialkylstannyl sulfide (PhSSnR$_3$) (Scheme **6**) [15]. In the manuscript, they proposed that the first step of the reaction was the generation of vinyl palladium bromide species by the reaction of 1-alkenyl bromides with low-valent palladium species [16]. From above results disclosed in Schemes **4** and **5** and the proposal reaction pathway disclosed in Rossi's report, it was suggested that the oxidative addition of aryl iodide to low valent palladium species is the first step of the coupling reaction. A possible reaction path for this reaction is shown in Scheme **7**. The first step involves the oxidative addition of the aryl iodides to the low-valent palladium species to form an aryl palladium iodide species (**4**). The following ligand exchange of **4** with PhSeSnBu$_3$ (**1**) generates intermediate **5**. The subsequent reductive elimination from **5** affords the coupling product (**3**) and regenerates the low-valent species.



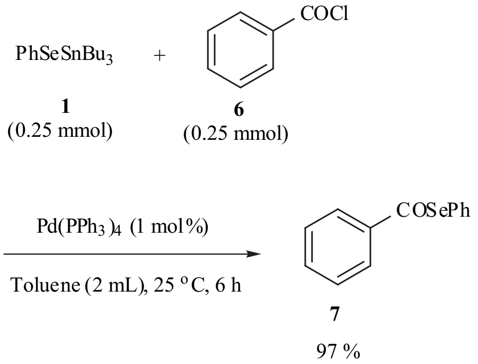
Scheme 6.



Scheme 7. A possible reaction path.

2-2. Synthesis of *Se*-Phenyl Selenol Esters [17, 18]

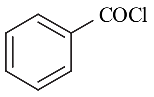
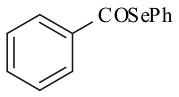
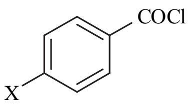
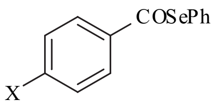
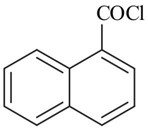
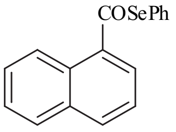
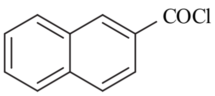
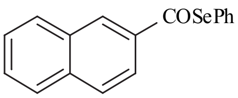
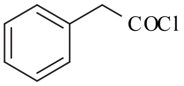
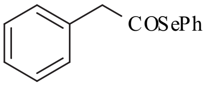
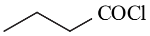
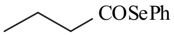
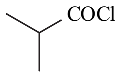
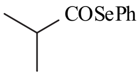
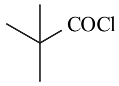
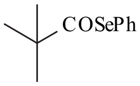
The development of a convenient and efficient method for the synthesis of *Se*-phenyl selenol esters has attracted considerable attention because they are useful transfer reagents for acyl or aroyl groups onto the various organic compounds [19]. When phenyl tributylstannyl selenide (**1**) was allowed to react with benzoyl chloride (**6**) in the presence of a catalytic amount of Pd(PPh$_3$)$_4$ at 25 °C for 6 h, *Se*-phenyl seleno benzoate (**7**) was formed in 97 % yield (Scheme **8**). The treatment of 4-methyl-, 4-methoxy-, 4-chloro-, 4-nitro- and 4-cyanobenzoyl chlorides under reaction conditions similar to that for benzoyl chloride afforded the corresponding *Se*-aryl selenol esters in 71-91 % yields (Table **2**). In the reaction of 1- and 2-naphthyl acid chlorides, the coupling reaction also proceeded to give *Se*-phenyl selenol esters in 87 and 92 % yields, respectively. 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 85 and 92 % yield. However, in the case of α-methyl- and α,α-dimethyl-substituted acyl chloride, the yields of product were slightly decreased.



Scheme 8.

In the coupling reaction of PhSeSnBu$_3$ (**1**) with aroyl or acyl chloride, the catalytic reaction pathways involving aroyl or acyl palladium intermediate (**8**), which is one of the active species, was proposed. It was known that aryl palladium complex is easily converted to the aroyl palladium complex under an atmosphere of carbon monoxide [20]. Thus, it is of much interest that the reaction of **1** with aryl halide is carried out under the pressurized of carbon monoxide because there is a possibility that it may cause an efficiently method for the synthesis of *Se*-aryl selenol esters. When phenyl tributylstannyl selenide (**1**) was allowed to react with iodobenzene (**2**) in the presence of a catalytic amount of Pd(PPh$_3$)$_4$ under the pressurized of carbon monoxide (5 atom) at 80 °C for 5 h, *Se*-phenyl selenobenzoate (**7**), in which **1** was coupled with **2** and carbon monoxide, was formed in 89 % yield (Scheme **9**).

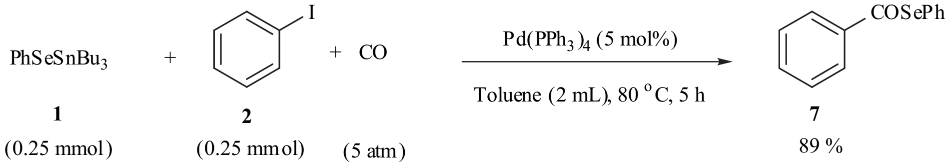
Table 2. Synthesis of Various *Se*-Phenyl Selenol Esters[a)]

Entry	RX	Product	Yield/%[b)]
1			97
			
2	X = CH_3		83
3	X = OCH_3		80
4	X = Cl		91
5	X = NO_2		83
6	X = CN		71
7			87
8			92
9			92
10			85
11			74
12			51

[a)] Reaction conditions. $PhSeSnBu_3$ (1) (0.25 mmol), aroyl or acyl chloride (0.25 mmol), $Pd(PPh_3)_4$ (1 mol%) and toluene (2 mL) at 25 °C for 6 h. [b)] GC yield.

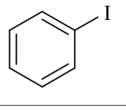
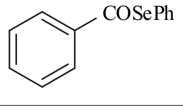
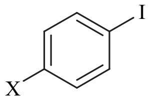
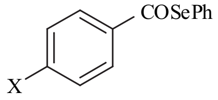
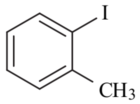
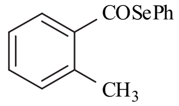
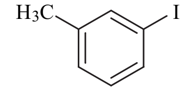
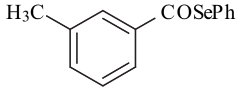
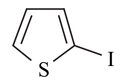
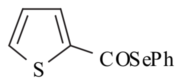
ArCO-PdL$_n$-Cl
8

Although the coupling reaction also took place even at atmospheric pressure of carbon monoxide, yield of **7** (55 %) was decreased due to the formation of diphenyl selenide as a by-product (20 %). Representative results of the synthesis of *Se*-aryl selenol esters by the coupling of **1**, aryl halide and carbon monoxide are indicated in Table **3**. 1-Iodo-3-methyl- and 1-iodo-4-methyl- and 1-iodo-4-methoxybenzene gave the corresponding selenol esters in 67, 73 and 70% yields, respectively. However, for the sterically congested substrate such as 1-iodo-2-methylbenzene, the yield of selenol ester was slightly decreased. For the reaction of 1-chloro-4-iodobenzene, the chloro group remained unchanged during the coupling process. *Se*-Phenyl 2-thiophene selenobenzoate was also obtained by the reaction of **1** with **2**-iodothiophenene and carbon monoxide in 68 % yield. For this reaction, the chloro- and bromobenzene did not give *Se*-



Scheme 9.

Table 3. Synthesis of Various *Se*-Pheneyl Selenol Esters[a)]

Entry	RX	Product	Yield/%[b)]
1			89
			
2	X = CH_3		73
3	X = OCH_3		70
4	X = Cl		85
5	X = NO_2		41
6			57
7			67
8			68

[a)]Reaction conditions. $PhSeSnBu_3$ (**1**) (0.25 mmol), aryl iodide (0.25 mmol), $Pd(PPh_3)_4$ (5 mol%), CO (5 atm) and toluene (2 mL) at 80 °C for 6 h. [b)]GC yield.

phenyl benzoate under the same reaction conditions as that of iodobenzene.

2-3. Synthesis of α-Phenylseleno Carbonyl Compounds [21]

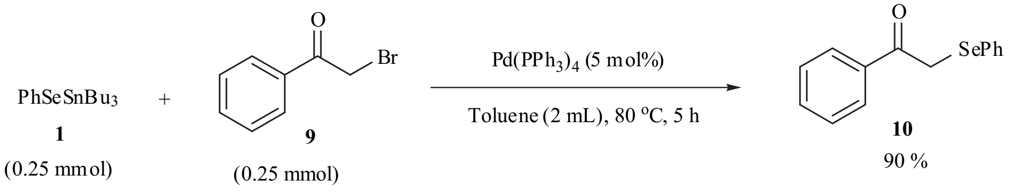
α-Phenylseleno carbonyl compounds were useful intermediates for the generation of the enolate anion and α-carbonyl carbon radical in organic synthesis, and much effort is being devoted to accomplish the synthesis of α-phenylseleno carbonyl compounds [21]. When **1** was allowed to react with α-bromoacetophenone (**9**) in the presence of $Pd(PPh_3)_4$ at 80 °C for 6 h, α-phenylseleno acetophenone (**10**) was obtained in 90 % yield (Scheme **10**).

Similarly, the palladium complex catalyzed the coupling of 4-methyl-, 4-cyano-, 4-chloro-, and 4-nitro-α-bromoacetophenone to give the corresponding α-phenylselenoacetophenones in moderate yields (Table **4**). For 4-methoxy-α-bromoacetophenone, the yield of product was improved by elevating the reaction temperature (110 °C). In this coupling reaction, the yields of products were influenced by the steric effect of the α-position.

Although the coupling reaction of **1** with α-bromopropiophenone gave α-phenylselenopropiophenone in 84 % yield, in the case of α-bromo-α-methylpropiophenone, the yield of α-phenylseleno ketone was low compared with α-bromopropiopehnone. An α-bromo dialkyl ketone such as 2-bromo-3-pentanone as well as α-bromoalkyl phenyl ketones was coupled with **1** giving 2-phenylseleno-3-pentanone in 48 % yield. Similarly, α-phenylseleno esters were successfully synthesized by the palladium-catalyzed reaction of **1** with α-bromo esters.

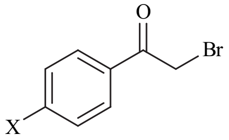
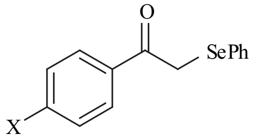
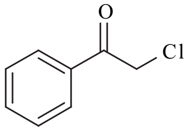
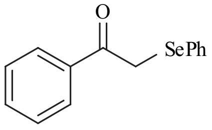
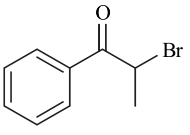
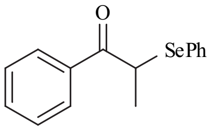
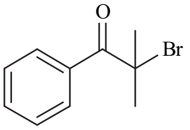
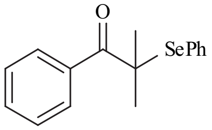
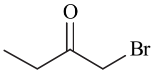
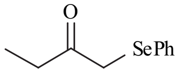
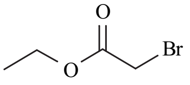
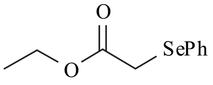
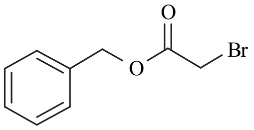
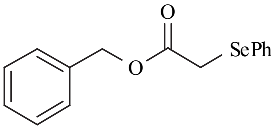
3. LEWIS ACID ASSISTED REACTION OF PHENYL TRIBUTYLSTANNYL SELENIDE WITH OXYGEN-CONTAINING COMPOUNDS

As the other methods of the synthesis of organoselenium compounds by the use of phenyl tributylstannyl selenide as a phenylselenated agent, we examined the reaction of phenyl



Scheme 10.

Table 4. Synthesis of Various α-Phenylseleno Carbonyl Compounds[a)]

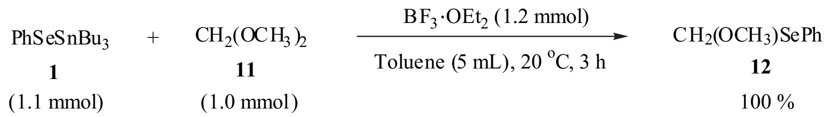
Entry	$RCOCH_2X$	Product	Yield/%[b)]
			
1	X = H		90
2	X = CH_3		60
3[c)]	X = OCH_3		46
4	X = Cl		43
5	X = NO_2		50
6	X = CN		46
7			22
8			84
9			22
10			48
11			56
12			52

a)Reaction conditions. $PhSeSnBu_3$ (**1**) (0.25 mmol), organic halide (0.25 mmol), $Pd(PPh_3)_4$ (5 mol%) and toluene (2 mL) at 80 °C for 6 h. b)GC yield. c)At 110 °C.

tributylstannyl selenide ($PhSeSnBu_3$) with oxygen-containing compounds in the presence of Lewis acid, and found that organoselenium compounds were obtained in moderate to good yields.

3-1. Reaction of Phenyl Tributylstannyl Selenide with Acetals [22]

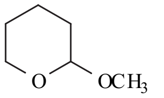
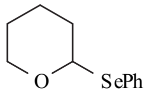
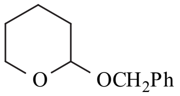
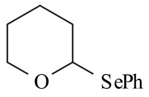
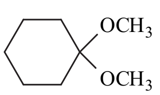
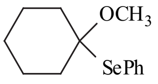
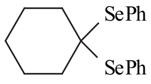
The treatment of phenyl tributylstannyl selenide ($PhSeSnBu_3$) (**1**) and dimethoxy-methane (**11**) in presence of $BF_3•OEt_2$ in toluene solvent at 20 °C for 3 h gave 1-methoxy-1-phenylseleno methane (**12**) in almost quantitatively yield (Scheme **11**). In the case of the other Lewis acids such as $AlCl_3$, $TiCl_4$ and $SnCl_4$, the yields and selectivities for monoselenoacetal over diselenoacetal were lower than that of $BF_3•OEt_2$. Use of dichloromethane, ether and acetonitrile as a solvent also gave the less satisfactory results. The results obtained for a wide variety of acetals are shown in Table **5**. Acetals derived from aliphatic aldehydes were converted into the corresponding monoselenoacetals in moderate to good yields, whereas benzaldehyde dimethyl acetal produced diselenoacetal, in preference to monoselenoacetal. Similarly, $BuSeSnBu_3$ served as a butylselenolated agent. The reaction proceeded with cyclic ethers having α-alkoxy substituent. Of special interest is that methoxymethyl (MOM) ether is converted into the



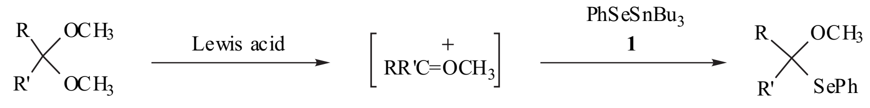
$$\underset{\substack{\mathbf{1} \\ (1.1\ \text{mmol})}}{\text{PhSeSnBu}_3} + \underset{\substack{\mathbf{11} \\ (1.0\ \text{mmol})}}{\text{CH}_2(\text{OCH}_3)_2} \xrightarrow[\text{Toluene (5 mL), 20 °C, 3 h}]{\text{BF}_3\cdot\text{OEt}_2\ (1.2\ \text{mmol})} \underset{\substack{\mathbf{12} \\ 100\ \%}}{\text{CH}_2(\text{OCH}_3)\text{SePh}}$$

Scheme 11.

Table 5. Synthesis of Monoselenoacetals[a)]

Entry	Acetal	Products (Yield/%)[b)]	
1	$CH_2(OCH_3)_2$	$CH_2(OCH_3)SePh$ (100)[c)]	
2	$CH_2(OC_2H_5)_2$	$CH_2(OC_2H_5)SePh$ (76)	
3[d)]	$CH_2(OC_2H_5)_2$	$CH_2(OC_2H_5)SeC_4H_9$ (76)	
4	$CH_3CH(OCH_3)_2$	$CH_3CH(OCH_3)SePh$ (44)	
5	$C_7H_{15}CH(OCH_3)_2$	$C_7H_{15}CH(OCH_3)SePh$ (50)	
6	$PhCH(OCH_3)_2$	$PhCH(OCH_3)SePh$ (12)	$PhCH(SePh)_2$ (43)
7[e)]		 (42)	$HOC_4H_8CH(OCH_3)SePh$ (20)
8[e)]		 (39)	$HOC_4H_8CH(OCH_2Ph)SePh$ (33)
9	$C_6H_{13}OCH_2OCH_3$	$C_6H_{13}OCH_2SePh$ (50)	$PhSeCH_2OCH_3$ (13)
10[f)]		 (42)	 (13)

[a)] Reaction conditions: $PhSeSnBu_3$ (1.1 mmol), acetal (1.0 mmol), $BF_3\cdot OEt_2$ (1.2 mmol) and toluene (5 mL) at 20 °C for 3 h. [b)] Isolated yield based on acetal. [c)] GC yield. d) $BuSeSnBu_3$ was used. [e)] -20 °C, 3h. [f)] -78 °C, 3h.



11 **13** **12**

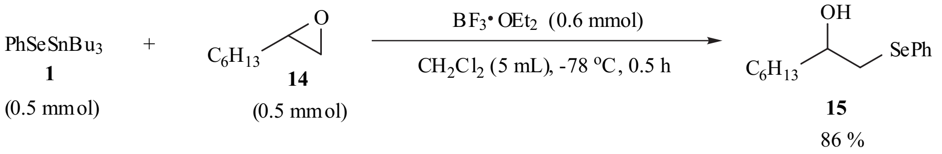
Scheme 12.

corresponding phenylselenomethyl ether in good selectivity. Although the reaction pathway is not fully understood, the course of the reaction may be suggested as Scheme **12**. Acetal (**11**) was reacted with Lewis acid to form an oxonium ion (**13**), on which subsequent reaction with phenyl tributylstannyl selenide (**1**) gives the corresponding monoselenoacetal (**12**).

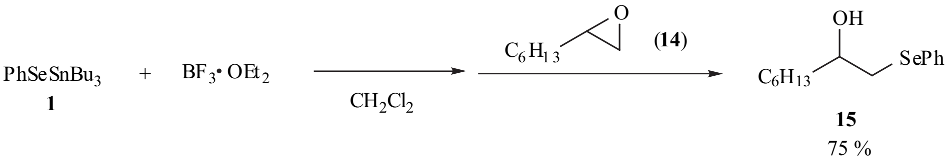
3-2. Reaction of Phenyl Tributylstannyl Selenide with Epoxides [23]

When phenyl tributylstannyl selenide (**1**) were allowed to react with 1,2-epoxyoctane (**14**) in the presence of Lewis acid, the ring opening reaction of **14** proceeded with complete regioselectivity to afford 1-(phenylseleno)-2-octanol (**15**) in 86 % yield (Scheme **13**). In this reaction, the yield of the product is significantly influenced by the order of the addition of **1** and the epoxide. The reaction of **1** with BF_3•OEt_2 in CH_2Cl_2 followed by the addition of the 1,2-epoxyoctane (**14**) provided 1-(phenylseleno)-2-octanol (**15**) in 75 % yield (Scheme **14**). In contrast, when BF_3•OEt_2 was first added to the CH_2Cl_2 solution of the **14** followed by the addition of **1**, starting materials were almost quantitatively recovered (Scheme **15**). The typical results of the reaction of **1** with epoxides in the presence of BF_3•OEt_2 at –78 °C are shown in Table **6**. When **1** was reacted with 1,2-epoxypropane and 1,2-epoxy-2-methyl-propane, 1-phenylseleno-2-hydroxyalkanes were obtained in 67 and 65 %

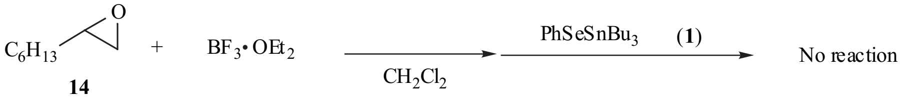
yields, respectively, with complete regioselectivity. The reaction of **1** with 1,2-epoxycyclohexane or *cis*-2,3-epoxybutane stereospecifically gave *trans*-2-(phenylseleno) cyclohexanol or *threo*-3- (phenylseleno)-2-butane in moderate yields. The conversion of 1,2-epoxyhexene and 1,2-epoxy-3-phenoxypropane to the corresponding β-hydroxy phenylselenides was successfully achieved without affecting the carbon-carbon double bond and ether functions. It is interesting to note that the epoxide having a hydroxyl group was also converted into the corresponding *vic*-diol derivative



Scheme 13.

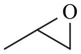
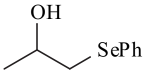
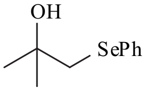
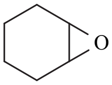
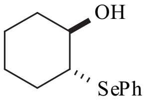
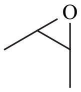
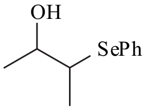
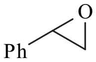
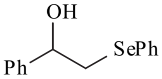
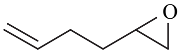
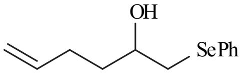
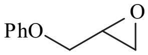
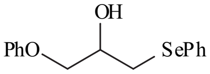
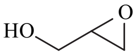
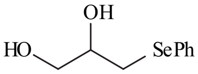


Scheme 14.



Scheme 15.

Table 6. Synthesis of β-Hydroxy Phenylselenides[a)]

Entry	Epoxide	Product	Yield/%[b)]
1			67
2			65
3			39
4			60[c)]
5			87
6			78
7			50
8			60

[a)] Reaction conditions: $PhSeSnBu_3$ (0.5 mmol), epoxide (0.5 mmol), $BF_3 \cdot OEt_2$ (0.6 mmol) and CH_2Cl_2 (5 mL) at -78 °C for 0.5 h. [b)] Isolated yield. [c)] Threo isomer was obtained.

in moderate yield. The conversion of styrene oxide to the corresponding β–hydroxy phenylselenide has already been described, however, there are few examples on the regioselective ring opening reaction of styrene oxide with organoselenium compounds. In the present case, the reaction of **1** with styrene oxide proceeded with complete regioselectivity to afford 1-phenyl-2-(phenylseleno)-ethanol in 87 % yield.

4. SUMMARY

New methods for the synthesis of organoselenium compounds by the use of phenyl tributylstannyl selenide as a phenylselanated reagent have been developed. The reaction of phenyl tributylstannyl selenide with aryl or alkyl halides, acid chlorides or α-bromo ketones or esters in the presence of palladium complex catalyst gave the corresponding aryl or alkyl phenyl selenide, selenol esters or α-phenylseleno ketone or esters in moderate to good yields. The reaction of aryl iodide with phenyl tributylstannyl selenide is applicable to the synthesis of selenol esters when the reaction was carried out under the pressure of carbon monoxide. Organoselenium compounds were also synthesized by the reaction of phenyl tributylstannyl selenide with oxygen-containing compounds such as acetals or epoxides in the presence of $BF_3•OEt_2$.

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[4] The bond energy of the Se-Sn bond is $D_{298}{}^0$ = 98.2 + 3 kcal/mol. See: Ho. K. C. M. In *Thermodynamic Data for Inoganic Sulfides, Selenides, and Tellurides*; Rechhood Press: England, **1974**; p 594.

[5] The other application of organoselenium compounds having a Se-Sn bond are very few [6-12].

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