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Synthesis of selenol esters: palladium-catalyzed coupling of phenyl tributylstannyl selenide with aryl iodides and carbon monoxide

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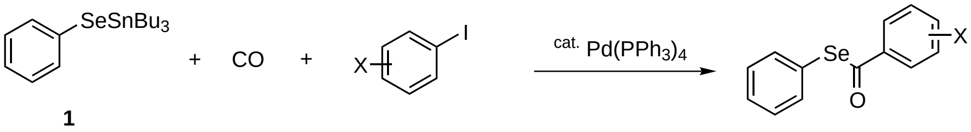
Abstract—It was found that palladium complex catalyzed three-component coupling of phenyl tributylstannyl selenide with aryl iodides and carbon monoxide to afford the corresponding selenol esters in moderate to good yields. © 2002 Elsevier Science Ltd. All rights reserved.

The development of a convenient and efficient method for the synthesis of selenol esters has attracted considerable attention because they are useful transfer reagents for acyl or aroyl groups onto the various organic compounds.[1–3] Although various synthetic methods of selenol esters have been reported,[8] there are some disadvantages: (i) handling of organoselenium compounds which are unstable in air and moisture; (ii) difficulty of preparation of organoselenium compounds; (iii) the utilization of acid chlorides which are easily hydrolyzed by water, and (iv) strongly basic or acidic reaction conditions.

We have recently reported that the coupling reaction of phenyl tributylstannyl selenide, $PhSeSnBu_3$ (**1**), which is a stable reagent in air and moisture, with aryl and alkyl halides in the presence of palladium catalyst efficiently proceeded under neutral condition to give the corresponding diorganyl selenides in moderate to good yields.[9,10] In the course of our study on the utilization of **1** in organic synthesis, we have developed the synthetic method of selenol esters using a three-component coupling reaction of **1** with aryl iodides and carbon monoxide under neutral conditions (Scheme 1).[11,12]

When phenyl tributylstannyl selenide (**1**) was allowed to react with iodobenzene (**2**) in the presence of a catalytic amount of $Pd(PPh_3)_4$ in toluene solution under the pressure of carbon monoxide (5 atm) at 80°C for 5 h, Se-phenyl selenobenzoate (**3**), in which **1** was coupled with **2** and carbon monoxide, was formed in 89% yield (entry 1 in Table 1).[15] For the reaction at a lower reaction temperature (50°C), the yield of **3** was slightly decreased (entry 2). A pressure decrease of carbon monoxide led to a decrease in the yield of **3** due to the formation of diphenyl selenide as a by-product (entry 3). For this reaction, the chloro- and bromobenzenes did not give **3** under the same reaction conditions as that of **2**. Table 1 shows the results of the palladium-catalyzed synthesis of various selenol esters by the reaction of **1** with aryl iodides and carbon monoxide. The reaction proceeded well even when *m*- and *p*-iodotoluene and *p*-iodoanisole were used as the aryl iodides giving the corresponding selenol esters in 67, 73 and



Scheme 1.

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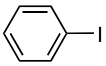
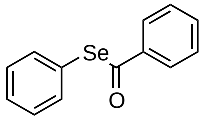
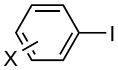
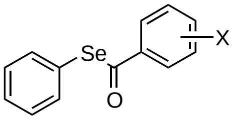
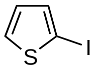
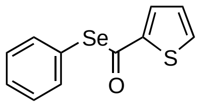
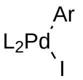
Table 1. Synthesis of various selenol esters[a]

Entry	Aryl Iodide	Selenol Ester	Yield / %[b]
1	 2	 3	89
2[c]	2	3	66
3[d]	2	3	55[e]
			
4[f]	X = *o*-CH$_3$		57
5	= *m*-CH$_3$		67
6	= *p*-CH$_3$		73
7	= *p*-CH$_3$O		70
8	= *p*-Cl		85
9[g]	= *p*-NO$_2$		41
10			68

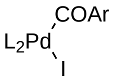
a) Reaction conditions: aryl iodide (0.25 mmol), 1 (0.25 mmol), Pd(PPh$_3$)$_4$ (5 mol%), CO (5 atm) and toluene (2 mL) at 80 °C for 5 h. b) GC yields. c) At 50 °C. d) CO (1 atm). e) PhSePh (20 %) was formed. f) CO (50 atm). g) CO (50 atm).

70% yields, respectively (entries 5–7). However, for the sterically congested substrate such as *o*-iodotoluene, the yield of selenol ester was slightly decreased (entry 4). For the reaction of *p*-chloroiodobenzene, the chloro group remained unchanged during the coupling process (entry 8). When **1** was allowed to react with *p*-nitroiodobenzene under the same reaction conditions as that of the iodobenzene, the yield was low. However, the yield was improved by the higher carbon monoxide (50 atm) pressure (entry 9). Se-Phenyl 2-thiopheneselenobenzoate was also obtained by the reaction of **1** with 2-iodothiophene and carbon monoxide in 68% yield (entry 10).

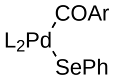
We have already shown that palladium complexes such as Pd(PPh$_3$)$_4$ act as a catalyst for the coupling reaction of aryl and alkyl halides with PhSeSnBu$_3$ (**1**) giving the corresponding diorganyl selenides in moderate to good yields under mild conditions.[9] It has been known that the aryl palladium complex (**4**) is easily converted to the aroyl palladium complex (**5**) under an atmosphere of carbon monoxide.[16,17] Based on these results, the catalytic reaction pathways involving aroyl palladium intermediate (**5**), which is one of the active species in this coupling reaction, was proposed. The first step involves the oxidative addition of the aryl iodide to the low-valent palladium species, followed by the insertion of carbon monoxide into the palladium-carbon to form the aroyl palladium complex (**5**). The following ligand exchange of **5** with PhSeSnBu$_3$ generates the intermediate **6**. The subsequent reductive elimination from **6** affords the selenol ester and regenerates the low-valent palladium species.


$L_2Pd(Ar)(I)$

4


$L_2Pd(COAr)(I)$

5


$L_2Pd(COAr)(SePh)$

6

In summary, we succeeded in the synthesis of a selenol ester by the reaction of PhSeSnBu$_3$ with aryl iodide and carbon monoxide. Further investigation on the utilization of PhSeSnBu$_3$ in organic synthesis is now in progress.

Acknowledgements

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