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Pummerer-type α-functionalization of arylseleninylacetates by treating with trimethylsilyl- or tri-*n*-butylstannyl-masked nucleophiles and trifluoroacetic anhydride or a Lewis acid

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Abstract

Arylseleninylacetates underwent facile α-functionalization on treatment with trimethylsilyl- or tri-*n*-butylstannyl-masked nucleophiles and trifluoroacetic anhydride (TFAA) or a Lewis acid. © 2000 Elsevier Science Ltd. All rights reserved.

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Recent interest in the field of organic heteroatom chemistry has been concentrated on heteroatom-stabilized carbenium ions, and several methods for α-functionalization of alkyl selenides, selenoacetals, α-haloselenides, or alkenyl selenides via chemically- or electrochemically-generated selonium ions **A** (X = Se) or α-selenocarbenium ions **B** (X = Se) have been reported to date.[1,2] However, the lability of seleninyl functionalities has caused serious limitation in the synthetic use of selenoxides in spite of their potentiality as synthetic equivalents of **A** or **B** (Scheme 1). It was expected that selenoxides **2**[3] bearing an alkyl chain on the selenium atom would undergo α-functionalization via **A** or **B** that might be generated through a Pummerer-type reaction,[4] by treating **2** with nucleophilic reagents. In this paper, we would like to describe an α-functionalization of selenoxides **2** by the combined treatment of nucleophiles masked with a trimethylsilyl or a tri-*n*-butylstannyl group and trifluoroacetic anhydride (TFAA) or a Lewis acid.

A CH_2Cl_2 solution of selenide **1a**–**b** was at first treated with mCPBA (1.1 mol amt.) through the usual procedure to give selenoxides **2a**–**b** as 1:1 epimeric mixtures.[3,5] Unexpectedly, treatment of **1c** or **1d** with mCPBA only gave the recovery of the compounds in almost quantitative yield due to deoxygenation during the usual reductive workup (aq. Na_2SO_3 solution), purification, or

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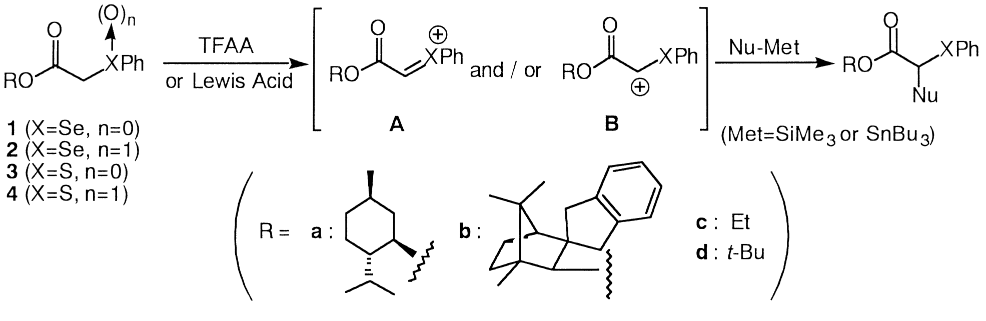


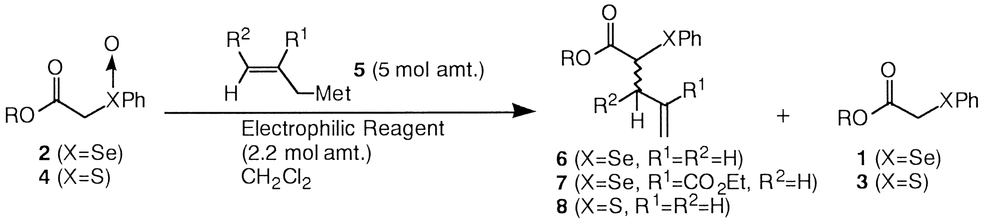
Scheme 1.

storage. These results indicated the effective kinetic protection of the seleninyl functionality of **2** by using the neighboring *l*-menthyloxycarbonyl moiety. Sulfoxides **4a**, **4c**, and **4d** were also prepared by similar treatment of sulfides **3** with mCPBA. Subsequently, when a CH_2Cl_2 solution of **2a** or sulfoxides, **4a**, **4c**, or **4d**, were treated with allyltrimethylsilane or allyltri-*n*-butylstannane (**5**, 5.0 mol amt.) and TFAA or $BF_3{\cdot}OEt_2$ (2.2 mol amt.), inseparable diastereomeric mixtures of α-allylation products, **6a**, **8a**, **8c**, or **8d**, respectively, were obtained in modest yields along with **1a** or **3** in each case. A similar treatment of **2a** with 2-ethoxycarbonylallyltrimethylsilane and $BF_3{\cdot}OEt_2$ also afforded **7a** predominantly. However, the use of acetic anhydride in place of TFAA for the reaction of **2a** only gave a diastereomeric mixture (about 1:1) of α-acetoxyselenide **14a** in 62% yield. The treatment of **2b** with the same reagents or the treatment of **2a** with TFAA and an allylsilane bearing an ethyl or a phenyl group at the γ-position only gave a complex mixture. These results suggested that the steric factor between the γ-position (R^2) of allylsilanes and the α-position of the phenylseleninyl group of **2** might affect the reaction course. In addition, treatment of a CH_2Cl_2 solution of **2a** with TFAA in the presence of an additive, such as cyclohexene, phenylacetylene, or anisole, only gave a complex mixture in which no products originated from electrophilic addition of these adducts were found.[1] A similar treatment of **2a** or **4c**–**d** with trimethylsilyl azide and TFAA also gave α-azidation products, **12a** or **13c**–**d**, respectively. All the results are shown in Tables 1 and 2.

However, one-pot treatment of a CH_2Cl_2 solution of **1a** with mCPBA, allyltrimethylsilane, and TFAA only gave a complex mixture containing diphenyl diselenide (**9**), selenide **1a**, allyl phenyl selenide (**10**), 1-trimethylsilyl-3-phenylseleno-2-propanol (**11**), and several unidentified products. ^1H NMR monitoring of the reaction of a $CDCl_3$ solution of **1a** with mCPBA (1.1 mol amt.) at 27°C exhibited the formation of a 1:1 diastereomeric mixture of selenurane **X** ($\delta = 3.83$, 3.85, 4.21, and 4.25 ppm for the non-equivalent four protons of the methylene groups of **X**) at the primary stage.[4d,6] However, the signals of **X** gradually disappeared within several minutes, and new signals of a diastereomeric mixture of α-acyloxyselenides **15a** were observed. Actually, **15a** was isolated as a stable compound and was unreactive toward the α-allylation.

Subsequently, when a $CDCl_3$ solution of **2a** was treated with TFAA and the reaction was monitored by ^1H NMR at 27°C, the formation of bis(trifluoroacetoxy)selenurane **Y** ($\delta = 4.70$ and 4.75 ppm for the non-equivalent geminal protons of the methylene group of **Y**) was observed at the primary stage.[6] But, selenurane **Y** caused facile decomposition within a few minutes into α-trifluoroacetoxyselenide **16a** in the $CDCl_3$ solution. Compound **16a** seemed stable enough in the solution but caused facile decomposition to give a complex mixture including **9**, **1a**, and several unidentified products, during the usual workup and purification. When a CH_2Cl_2 solution of **16a**,

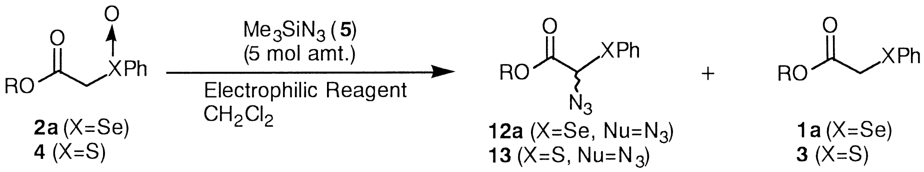
Table 1
α-Allylation of selenoxides **2** and sulfoxides **4** by treating with an allylating agent **5** and an electrophilic reagent



Substrate		Allylating Agent (**5**)			Electrophilic	Temp	Time	Yield / % [a]	
2,4	X	R^1	R^2	Met	Reagent	/ °C	/ h	**6, 7, 8**	**1, 3**
2a	Se	H	H	$SiMe_3$	$(CF_3CO)_2O$	0	3.5	42 (**6a**) [b]	27 (**1a**) [c]
2a	Se	H	H	$SiMe_3$	$BF_3{\bullet}OEt_2$	0	1	37 (**6a**) [b]	24 (**1a**) [c]
2a	Se	H	H	$SnBu_3$	$(CF_3CO)_2O$	0	1	33 (**6a**) [b]	30 (**1a**) [c]
2a	Se	H	H	$SiMe_3$	$(CH_3CO)_2O$	0	1	0 (**6a**)	0 (**1a**) [d]
2a	Se	CO_2Et	H	$SiMe_3$	$BF_3{\bullet}OEt_2$	Reflux	21	63 (**7a**) [b]	trace (**1a**)
4a	S	H	H	$SiMe_3$	$(CF_3CO)_2O$	-78	2	52 (**8a**) [e]	5 (**3a**)
4c	S	H	H	$SiMe_3$	$(CF_3CO)_2O$	-78	2	48 (**8c**)	6 (**3c**)
4d	S	H	H	$SiMe_3$	$(CF_3CO)_2O$	-78	5	46 (**8d**)	10 (**3d**)

[a] Isolated yields. [b] An inseparable epimeric mixture (about 1:1). [c] Diphenyl diselenide (**9**) was obtained in moderate yield. [d] α-Acetoxyselenide **14a** was obtained in 62% yield. [e] An inseparable epimeric mixture (about 3:2).

Table 2
α-Azidation of selenoxide **2a** or sulfoxides **4** by treating with trimethylsilyl azide (**5**) and TFAA

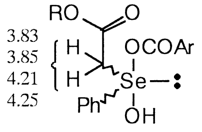


Substrate		Electrophilic	Temp	Time	Yield / % [a]	
2, 4	X	Reagent	/ °C	/ h	Product	**1**
2a	Se	$(CF_3CO)_2O$	-78	3.5	45 (**12a**) [b]	12 (**1a**) [c]
4c	S	$(CF_3CO)_2O$	0	3	76 (**13c**)	3 (**3c**)
4d	S	$(CF_3CO)_2O$	0	3	86 (**13d**)	3 (**3d**)

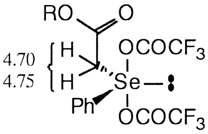
[a] Isolated yields. [b] An inseparable epimeric mixture (about 1:1). [c] Diphenyl diselenide (**9**) was obtained as main byproduct.

prepared preliminarily by adding TFAA (2 mol amt.) to a CH_2Cl_2 solution of **2a**, was treated with allyltrimethylsilane (5 mol amt.) at room temperature, only a complex mixture in which allylation products **6a** were found in rather low yield was obtained. These results indicated that isolation of selenoxides **2** was essentially required for the α-functionalization and that the reactions might occur only via selonium ions **Z** (or α-selenocarbenium ions **Z**′) generated through elimination of trifluoroacetic acid and trifluoroacetate ion from **Y**.[3,6] However, several attempts to detect **Z** or **Z**′ by NMR measurements were not successful at all.

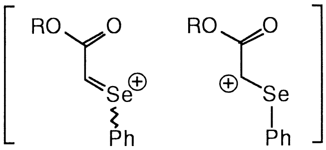
In conclusion, α-functionalization of selenoxides **2** was achieved by treating with silyl- or stannyl-masked nucleophilic reagents and TFAA or Lewis acid through the route including generation of intermediary selonium ions **Z** or α-selenocarbenium ions **Z′** via selenuranes **Y**. Further attempts for the synthetic applications of these reactions are in progress in our laboratory.



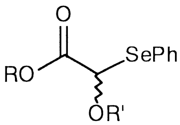
X (Ar=*m*-ClC$_6$H$_4$)



Y



Z **Z'**



14a (R'=CH$_3$CO)
15a (R'=*m*-ClC$_6$H$_4$CO)
16a (R'=CF$_3$CO)

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