

Scheme A

The Silicon-Selenium Exchange Reaction: A Convenient One-pot Procedure for Organoselenium Reactions¹

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The versatile utility of organoselenium reagents in organic synthesis has been proven during the last decade². However, their availability from commercial sources is rather limited because they deteriorate quite easily upon storage under the usual conditions. It is therefore desirable to have a simple, efficient, and rapid method of their preparation which uses commercially available organoselenium reagents and affords products which can be used directly in subsequent reactions without tedious isolation procedures.

In a previous communication³, we reported a convenient synthesis of phenyl selenocyanate (**1a**) based on the first silicon-selenium exchange reaction (Scheme A). We now report that this reaction can be extended to the synthesis of other organoselenium reagents. As shown in Scheme A, benzeneselenenyl chloride (**2**) reacts rapidly with trimethylsilyl derivatives (**3a-e**) at -78°C to room temperature to afford the corresponding selenium compounds **1a-e**.

The reactions of Scheme A proceed fast and in nearly quantitative yield as shown by ^{13}C -N.M.R. spectrometry. When the trimethylsilyl compound **3** is added to a cooled solution

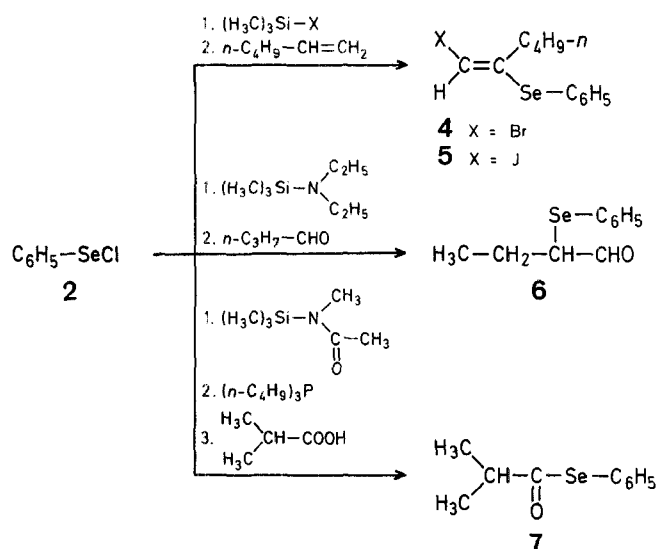
of an equimolecular amount of benzeneselenenyl chloride (**2**) in chloroform in an N.M.R. tube and the mixture is warmed to room temperature the signals of compounds **2** and **3** rapidly disappear to be replaced by new signals which are consistent with those expected for a 1/1 mixture of the ligand-exchanged product **1** and chlorotrimethylsilane; in all cases, no other products or starting materials can be detected by ^{13}C -N.M.R. spectroscopy.

Products **1b**, **c**, **d** were unequivocally identified by comparison with authentic samples prepared by known methods⁴. The structure of product **1e** derived from **2** and *N*-acetyl-*N*-methylaminotrimethylsilane (**3e**) was consistent with its N.M.R. data. The ^1H -N.M.R. spectrum of **1e** shows two sharp singlets at $\delta = 2.29$ (CO-CH₃) and 3.32 ppm (N-CH₃) and a broad singlet at $\delta = 7.26$ ppm (C₆H₅). The significant downfield shifts of the signals of the two methyl groups as compared with the corresponding signals of the starting silyl compound **3e** ($\delta = 2.06$ ppm for CO-CH₃ and 2.82 ppm for N-CH₃) clearly indicate that the silyl group in **3e** has been replaced by the phenylseleno group. The low-field shift of the methyl C-atoms of product **1e** (^{13}C -N.M.R.: $\delta = 41.9$ for N-CH₃ and 22.2 for CO-CH₃) relative to the signals of the C-atoms of **3e** ($\delta = 31.8$ for N-CH₃ and 22.0 ppm for CO-CH₃) is also in agreement with the structure **1e**. The ^{13}C -N.M.R. data of products **1a-e** are listed in the Table.

The synthesis of compounds **1a-e** according to Scheme A is performed in a flask which is connected to a vacuum line; after completion of the reaction, the flask is evacuated to remove all volatile materials. The residue is the almost pure selenium compound **1**.

In the present investigation, the selenium compounds **1b-e** were not further purified. Instead, they were directly subjected to the reaction with 1-hexyne, butanal, or tributylphosphine and 2-methylpropanoic acid to give products **4**, **5**, **6**, or **7**, respectively (Scheme B).

(*E*)-1-Bromo- and (*E*)-1-iodo-2-phenylseleno-1-hexene (**4** and **5**) were obtained as single stereoisomers⁵. Compound **4** was identified by microanalysis, spectral data (I.R., ^1H - and ^{13}C -N.M.R.), and an independent synthesis from **1b** (prepared from diphenyl diselenide and bromine⁶) and 1-hexyne. The structure of compound **5** was unambiguously established by an independent synthesis from **1c** (prepared from diphenyl diselenide and iodine⁷) and 1-hexyne. The structure of compound **6** was proven by comparison with an authentic sample prepared from **1d** (prepared according to Ref.⁹) and butanal. Our preparation of compound **6** (93% yield) seems



Scheme B

to be more efficient than the reported method⁸ which requires isolation of **1d**⁹. The structure of compound **7** was corroborated by microanalysis and spectral data. It is worthy of note that the reaction of *N*-phenylselenophthalimide with carboxylic acids, which is related to the preparation of **7**, has been reported previously¹³.

The quantitative formation of the selenium compounds **1a–e**, as revealed by N. M. R. spectroscopy as well as by their conversions, is not surprising if one considers that the driving force of the reaction may be the strong affinity of Si-atom toward chlorine (Si—Cl bond: 473 kJ/mol) which is much stronger than the affinity of the Si-atom toward the other groups (Si—CN bond: 373 kJ/mol; Si—Br bond: 402 kJ/mol; Si—I bond: 323 kJ/mol; Si—N bond: 419 kJ/mol)¹¹. A number of reactions of the same type have been reported recently¹².

In summary, we have shown that several synthetically important organoselenium reagents (**1**) can be easily and quantitatively prepared from benzeneselenenyl chloride (**2**) and silicon compounds (**3**), both of which are easily obtainable from commercial materials and that they can be used directly without isolation for subsequent reactions.

All glassware, syringes, needles, and stirring bars were oven-dried at 120 °C before use. Reactions were performed under inert conditions on a vacuum-argon double manifold line. Benzeneselenenyl chloride (**2**) was purchased from Aldrich Chemical Co., N. J., and used without further purification. Commercially available silicon compounds **3a–e** were distilled under argon before use. Tetrahydrofuran was distilled over sodium benzophenone ketyl under argon. Dichloromethane was distilled from calcium hydride and stored over 4 Å molecular sieves under argon. German Merck Kieselgel 60 (230–400 mesh) was used for all column-chromatographic separations. I. R. spectra were recorded on a JASCO A-102 Spectrometer. N. M. R. spectra on a JEOL FX-90Q Spectrometer.

Analytical-Scale Preparation of Selenium Compounds **1** in an N. M. R. Tube; General Procedure:

Benzeneselenenyl chloride (**2**; 57.5 mg, 0.300 mmol) is introduced in an oven-dried tube, which has been thoroughly purged with argon and stoppered with a serum cap. While the system is being kept under argon, deuteriated chloroform (0.5 ml) is injected by syringe and the dark red solution is cooled to –78 °C. To this is rapidly added the trimethylsilyl compound **3** (0.300 mmol) with the aid of a syringe and the mixture is stirred at room temperature using a vortex mixer. The ¹³C-N. M. R. data of these solutions are listed in the Table.

Table. ¹³C-Spectral Data of Compounds **1a–e** prepared from **2** and **3** by the Analytical-Scale Procedure and of Authentic Samples of **1a–e**

I	¹³ C-N. M. R. (CDCl ₃ /TMS _{int}) δ [ppm]		Assignment
	Prepared from 2 and 3	Authentic Samples ^a	
a	132.5 (d), 130.2 (d), 129.6 (d), 121.6 (s), 101.4 (s), 3.1 (q)	132.6 (d), 130.3 (d), 129.7 (d), 121.8 (s), 101.4 (s), 3.2 (q)	C ₆ H ₅ —CN (H ₃ C) ₃ SiCl
b	134.9 (d), 130.2 (d), 129.4 (d), 3.2 (q)	134.9 (d), 130.2 (d), 129.4 (d), 3.2 (q)	C ₆ H ₅ (H ₃ C) ₃ SiCl
c	133.9 (d), 129.3 (d), 128.8 (d), 3.3 (q)	133.7 (d), 129.4 (d), 129.1 (d), 3.2 (q)	C ₆ H ₅ (H ₃ C) ₃ SiCl
d	131.0 (d), 128.5 (d), 126.9 (d), 53.8 (t), 14.6 (q), 3.0 (q)	130.9 (d), 128.5 (d), 126.9 (d), 53.7 (t), 14.5 (q), 3.2 (q)	C ₆ H ₅ CH ₂ CH ₃ (H ₃ C) ₃ SiCl
e	129.4 (d), 127.8 (d), 41.9 (q), 22.3 (q), 3.0 (q)	— — — — 3.2 (q)	C ₆ H ₅ N—CH ₃ CO—CH ₃ (H ₃ C) ₃ SiCl

^a Authentic samples of **1a–d** were prepared according to the reported procedures^{3,6,7,9}.

(*E*)-1-Bromo-2-phenylseleno-1-hexene (**4**):

Into a stirred solution of benzeneselenenyl chloride (**2**; 285 mg, 1.49 mmol) in tetrahydrofuran (5.0 ml) is injected, all at once, bromotrimethylsilane (**3b**, *d* = 1.17; 200 μl, 1.53 mmol) at 78 °C under argon. The mixture is stirred at room temperature for 15 min. The whole system is then evacuated at 0.1 torr for 30 min to remove all volatile materials. The dark-red crystalline residue is dissolved in tetrahydrofuran (5 ml). This solution is cooled to –78 °C, 1-hexyne (*d* = 0.715; 210 μl, 1.83 mmol) is added all at once at –78 °C, and stirring is continued at room temperature for 12 h. The mixture is then concentrated and the residue purified by column chromatography on silica gel using hexane as eluent to afford product **4** as a colorless oil; yield: 455 mg (96 %).

C₁₂H₁₅BrSe calc. C 45.31 H 4.75 Br 25.12
(318.1) found 45.34 5.03 25.47

I. R. (neat): ν = 3080 (m); 1580 (m); 1021 (m); 738 (s); 690 (s) cm^{–1}.

¹H-N. M. R. (CDCl₃/TMS_{int}): δ = 7.3 (m, 5H_{arom}); 6.37 (s, 1H, =CH); 2.43 (t, 2H, *J* = 7 Hz, C=C—CH₂); 1.47 (m, 4H, CH₂—CH₂—CH₂—CH₃); 0.89 ppm (t, 3H, *J* = 7 Hz, CH₃).

¹³C-N. M. R. (CDCl₃/TMS_{int}): δ = 136.6 (s, =C—Se); 133.6 (d, C₆H₅); 129.3 (d, C₆H₅); 129.1 (s, C₆H₅); 127.9 (d, C₆H₅); 106.0 (d, =CH—Br); 34.8 (t, CH₂); 29.8 (t, CH₂); 22.1 (t, CH₂); 13.8 ppm (q, CH₃).

(*E*)-1-Iodo-2-phenylseleno-1-hexene (**5**):

Iodotrimethylsilane (**3c**, *d* = 1.470; 204 μl, 1.50 mmol) is injected into a stirred solution of benzeneselenenyl chloride (**2**; 274 mg, 1.43 mmol) in dichloromethane (5.0 ml) [tetrahydrofuran cannot be used as solvent because it reacts with **3c**]¹³ at –78 °C under argon. From this point on, the procedure describing the preparation of **4** is followed. Product **5** is obtained as a light yellow oil; yield: 511 mg (98 %).

C₁₂H₁₅ISe calc. C 39.48 H 4.14 I 34.76
(365.1) found 39.69 4.48 34.75

I. R. (neat): ν = 3075 (m); 1580 (m); 1021 (m); 735 (s); 690 (s) cm^{–1}.

¹H-N. M. R. (CDCl₃/TMS_{int}): δ = 7.3 (m, 5H_{arom}); 6.27 (s, 1H, =CH); 2.42 (t, 2H, *J* = 7 Hz, C=C—CH₂); 1.47 (m, 4H, CH₂—CH₂—CH₂—CH₃); 0.90 ppm (t, 3H, *J* = 7 Hz, CH₃).

¹³C-N.M.R. (CDCl₃/TMS_{int}): δ = 140.4 (s, =C—Se); 134.3 (d, C₆H₅); 129.4 (d, C₆H₅); 129.4 (s, C₆H₅); 128.1 (d, C₆H₅); 77.3 (d, =CH—J); 39.0 (t, CH₂); 30.0 (t, C—H₂); 22.1 (t, CH₂); 13.9 ppm (q, CH₃).

2-(Phenylseleno)-butanal (6):

Diethylaminotrimethylsilane (**3d**, d = 0.763; 516 μl, 2.7 mmol) is injected into a stirred solution of benzeneselenenyl chloride (**2**; 546 mg, 2.6 mmol) in tetrahydrofuran (10 ml) at –78°C. Stirring at –78°C is continued for 10 min and the mixture then allowed to warm to room temperature. The whole system is evacuated at 0.1 torr for 10 min to remove all volatile materials. Dry tetrahydrofuran (10 ml) is injected into the residue and the slightly yellow mixture stirred for 10 min at room temperature. While the mixture is being cooled at –78°C, butanal (d = 0.817; 230 μl, 2.6 mmol) is injected all at once and the mixture stirred for 30 min at room temperature. It is then diluted with ether (100 ml), washed with saturated sodium chloride solution (80 ml), dried with magnesium sulfate, and concentrated in vacuo. The oily residue is purified by medium-pressure column chromatography on silica gel eluting with hexane/dichloromethane (1/1) to afford **6** as a colorless oil; yield: 550 mg (93%).

C₁₀H₁₂OSe calc. C 52.87 H 5.32
(227.2) found 52.80 5.50

I.R. (neat): ν = 3060 (m); 2715 (w); 1717 (vs); 1578 (m); 738 (s); 690 (s) cm^{–1}.

¹H-N.M.R. (CDCl₃/TMS_{int}): δ = 9.38 (d, 1H, J = 3 Hz, CH=O); 7.3 (m, 5H_{arom}); 3.49 (dt, 1H, J = 3 and 7 Hz, CH—Se); 1.8 (m, 2H, CH₂); 1.06 ppm (t, 3H, J = 7 Hz, CH₃).

¹³C-N.M.R. (CDCl₃/TMS_{int}): δ = 193.0 (d, CHO); 135.8 (d, C₆H₅); 129.2 (d, C₆H₅); 128.7 (d, C₆H₅); 126.0 (s, C₆H₅); 54.7 (d, C—2); 21.3 (t, C—3); 12.6 ppm (q, C—4).

Se-Phenyl 2-Methylpropaneselenoate (7):

N-Acetyl-N-methylaminotrimethylsilane (**3e**, d = 0.901; 360 μl, 2.23 mmol) is added within 3 min to a stirred solution of benzeneselenenyl chloride (**2**; 372 mg, 1.94 mmol) in tetrahydrofuran (7.0 ml) at 0°C. The flask is then evacuated at 0.1 torr for 10 min to remove volatile materials. The residue is dissolved in tetrahydrofuran (5.0 ml), and tributylphosphine (392 mg, 1.94 mmol) is added within 5 min with stirring at 0°C. Stirring is continued at 0°C for 10 min. The mixture is then cooled to –78°C and a solution of 2-methylpropanoic acid (d = 0.964; 177 μl, 1.94 mmol) in tetrahydrofuran (1.0 ml) is added all at once and the mixture is allowed to warm to room temperature. Stirring is continued for 1 h and the mixture then quenched with water (50 ml) and extracted with ether (3 × 50 ml) to give product **7** as a colorless oil; yield: 126 mg (91%).

C₁₀H₁₂OSe calc. C 52.87 H 5.32
(227.2) found 52.57 5.60

I.R. (neat): ν = 3070 (w); 1723 (vs); 942 (vs); 843 (s); 738 (s); 690 (s) cm^{–1}.

¹H-N.M.R. (CDCl₃/TMS_{int}): δ = 7.42 (m, 5H_{arom}); 2.89 (sept, 1H, J = 7 Hz, —CH—); 1.23 ppm (d, 6H, J = 7 Hz, 2 CH₃).

¹³C-N.M.R. (CDCl₃/TMS_{int}): δ = 204.5 (s, C=O); 135.9 (d, C₆H₅); 129.2 (d, C₆H₅); 128.6 (d, C₆H₅); 126.4 (s, C₆H₅); 46.6 (d, CH); 19.0 ppm (q, CH₃).

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