Convenient Transformation of Benzyl Alcohol into Its Corresponding Selenide Using the Selenolate Anion–Aluminum Chloride Combination System

Hitoshi ABE,* Akira YAMASAKI, Hiroyuki FUJII, and Takashi HARAYAMA*

Faculty of Pharmaceutical Sciences, Okayama University, Okayama 700, Japan.

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Treatment of benzyl alcohol with a new reagent system, benzene- or methaneselenolate anion–aluminum chloride, yielded the corresponding selenide. The one-pot conversion of benzaldehyde into benzyl selenide was also achieved by this system.

Key words selenolate anion; benzyl alcohol; aluminum chloride

Organoselenium compounds have been widely used for organic synthesis because of their versatility.[1] Thus, a number of selenium-containing reagents have been developed to introduce a selenium group into organic molecules.[2] Electrophilic selenium reagents such as selenenyl halide, diselenide, selenocyanate[3] and selenophthalimide[4] are frequently used. Alternatively, nucleophilic reagents such as selenol[5] and selenolate anions[6] can also be used effectively to obtain several types of organoselenium compounds. The cleavage of the C–O bonds of cyclic ethers and esters, the conjugated addition to enones, and the diselenoacetalization of ketones, as well as the substitution of alkyl halides with selenol or selenolate anions, have been reported.[7]

In the course of our study on the cleavage of ether bonds using a selenolate anion, we unexpectedly isolated a small amount of bis selenide **1** from the reaction of tetrahydrofuran (THF) with methaneselenolate anion in the presence of aluminum chloride (Chart 1). The structure of **1** was elucidated by comparison with the spectral data of a product which was obtained from the reaction of 1,4-dibromobutane with methaneselenolate. We thought that the selenide **1** was generated by attack of a second methaneselenolate anion on the mono selenide **2**, in which aluminum chloride is coordinated to the oxygen of the alcohol. Thus, we thought that the selenolate anion–aluminum chloride combination system might be useful for the conversion of alcohols into the corresponding selenides in a direct manner. To our knowledge, there is no method available for the direct transformation of a hydroxy group into a selenenyl group, except for Grieco's method.[8] In this paper, we wish to report that a novel system, the selenolate anion–aluminum chloride system, can efficiently convert hydroxy groups into selenenyl groups in one step.

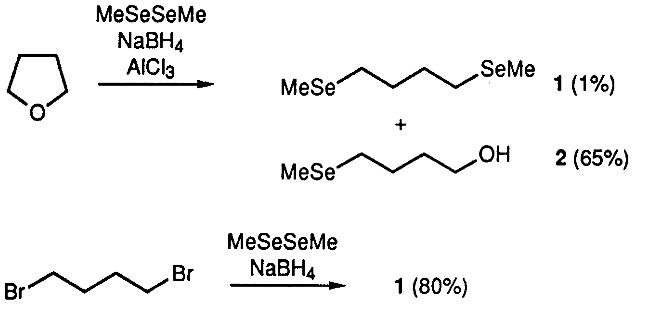
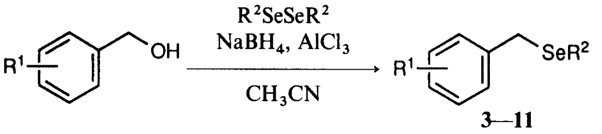


Chart 1

Selenolate anions were generated by the reductive cleavage of diselenides with sodium borohydride in acetonitrile. Reaction of benzyl alcohol with benzeneselenolate anion in the presence of aluminum chloride gave benzyl phenyl selenide (**3**), as shown in Table 1. An optimum yield was obtained by using 10 mol eq of sodium borohydride and 10 mol eq of aluminum chloride (entries 1—3). Reactions of some benzyl alcohols with benzene- or methaneselenolate anion were also investigated. Methaneselenolate seemed to be more suitable for this substitution reaction than benzeneselenolate (entries 6 and 7 *vs.* 11 and 12), with the exception of *p*-methoxybenzyl alcohol (entries 4 *vs.* 9 and 10). Interestingly, the reagents of this system do not affect methyl ether, in contrast to the thiol–aluminum chloride system (entries 4, 5, 9, 10).[9]

Next, we examined the reactions of other alcohols with methaneselenolate anion (Table 2). While benzylic type alcohols yielded the corresponding selenides **12—15** in moderate amounts (30—74%), non benzylic alcohols yielded only the starting materials or complex mixtures (entries 2, 3).

Table 1. Reaction of Primary Benzylic Alcohols



3—11

Entry	R^1	R^2	$NaBH_4$ (mol eq)	$AlCl_3$ (mol eq)	Time (h)	Product	Yield[a] (%)
1	H	Ph	1.3	10	5.0	**3**	6 (—)[b]
2	H	Ph	10	1.3	4.0	**3**	0 (82)
3	H	Ph	10	10	4.5	**3**	40 (21)
4	*p*-OMe	Ph	10	10	2.0	**4**	74 (0)
5	*m*-OMe	Ph	10	10	3.5	**5**	36 (32)
6	*p*-Cl	Ph	10	10	3.5	**6**	38 (13)
7	*p*-Me	Ph	10	10	3.5	**7**	44 (13)
8	H	Me	10	10	4.0	**8**	42 (27)
9	*p*-OMe	Me	1.4	1.8	3.0	**9**	71 (5)
10	*p*-OMe	Me	10	10	3.0	**9**	62 (0)
11	*p*-Cl	Me	10	10	4.0	**10**	63 (10)
12	*p*-Me	Me	12	10	4.0	**11**	80 (13)

a) Values in parentheses are % yields of the alcohols recovered. *b*) Not determined.

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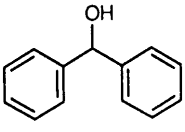
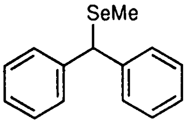
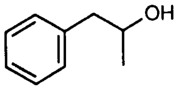
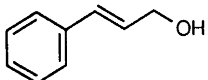
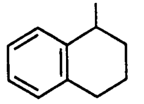
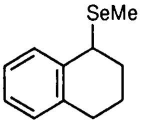
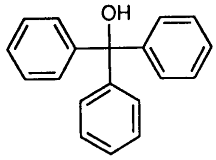
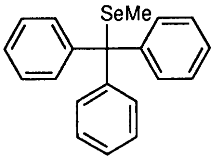
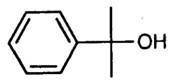
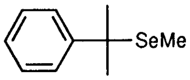
* To whom correspondence should be addressed.

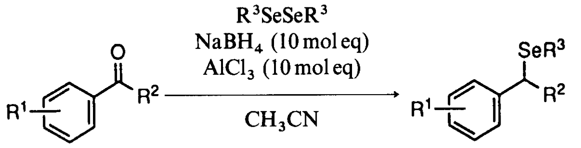
Table 2. Reaction of Various Alcohols with the Methyl Selenolate Anion

$$\text{alcohol} \xrightarrow[\text{CH}_3\text{CN}]{\substack{\text{MeSeSeMe} \\ \text{NaBH}_4\ (10\,\text{mol eq}) \\ \text{AlCl}_3\ (10\,\text{mol eq})}} \underset{\textbf{12—15}}{\text{selenide}}$$

Entry	Alcohol	Time (h)	Product	Yield[a)] (%)
1		3.5	 **12**	72 (3)
2		4.0	—	0 (92)
3		4.5	—[b)]	0 (8)
4		1.8	 **13**	74 (6)
5		4.5	 **14**	67 (15)
6		4.0	 **15**	30 (12)

a) Values in parentheses are % yields of the alcohols recovered. b) A complex mixture was obtained.

Table 3. Reaction of Carbonyl Compounds



Entry	R¹	R²	R³	Time (h)	Product	Yield[a)] (%)
1	H	H	Me	5.0	**8**	58 (10)
2	*p*-OMe	H	Ph	0.5	**4**	52 (6)
3	*p*-OMe	H	Me	0.5	**9**	51 (3)
4	*p*-Cl	H	Me	4.0	**10**	56 (32)
5	*p*-Me	H	Me	4.0	**11**	65 (11)
6	H	Ph	Me	3.5	**12**	66 (0)[b)]

a) Values in parentheses are % yields of benzyl alcohols. b) A 13% yield of diphenylmethane was obtained.

Because this reaction is carried out under highly reductive conditions, it is possible to transform carbonyl compounds into selenides in a single step. As shown in Table 3, treatment of benzaldehydes with a combination of selenolate anion and aluminum chloride in the presence of excess sodium borohydride yielded benzyl selenide derivatives (entries 1—5).[10,11] An attempt to convert benzophenone into diphenylmethyl methyl selenide was also successful (entry 6). In this case, 13% diphenylmethane was produced as a by-product.

As can be seen in Tables 1 and 2, the presence of a substituent which can stabilize the benzylic carbocation, such as an electron-donating group on the phenyl ring or a phenyl group at the benzylic position, increases the reactivity in this substitution reaction (entries 8 *vs.* 10—12, Table 1 and entry 8, Table 1 *vs.* entries 1 and 5, Table 2). Thus, it seems that the conversion of a hydroxy group into a selenenyl group proceeds *via* an $S_\mathrm{N}1$ type process.[12] However, the precise mechanism of this reaction is not clear at present.

In summary, we developed a novel system, the selenolate anion–aluminum chloride system, for the transformation of certain benzyl alcohols and benzaldehydes into benzyl selenides in one step. Further applications and studies on the mechanism of this reaction are under way.

Experimental

Melting points were measured with a Yanagimoto micro melting point hot-stage apparatus and are uncorrected. Infrared spectra (IR) were recorded on a JASCO A-102 spectrometer. Nuclear magnetic resonance spectra (NMR) were taken with a Varian VXR-200 or VXR-500 instrument in $CDCl_3$ with the chemical shifts being reported as δ ppm from tetramethylsilane as an internal standard, and couplings are expressed in hertz. Fast atom bombardment-mass spectra (FAB-MS) were obtained with a Shimadzu VG-70SE mass spectrometer. Silica-gel column chromatography was carried out with Wako-gel C-200 or Merck No. 9385, and Silica-gel 60 F254 plates (Merck No. 5744) were used for preparative TLC.

1,4-Bis(methylseleno)butane (1) and 4-Methylselenobutan-1-ol (2) A suspension of sodium borohydride (1.46 g, 38.7 mmol) and dimethyl diselenide (364 mg, 1.94 mmol) in dry acetonitrile (5 ml) was heated for 1 h under reflux. After this had cooled to room temperature, a solution of 1,4-dibromobutane (209 mg, 0.97 mmol) in dry acetonitrile (1 ml) was added and the whole was heated for 30 min under reflux, poured into a dilute aqueous HCl solution and extracted with dichloromethane. The extract was washed with brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a residue, which was subjected to silica-gel column chromatography with hexane–ethyl acetate (20 : 1) to yield **1** (190 mg, 80%) as a yellow oil. The analytical sample was further purified by preparative TLC. IR (neat) cm^{-1}: 2950, 1430. ^{1}H-NMR (500 MHz) δ: 1.77 (quint, 4H, $J=5.5$), 1.99 (s, 6H), 2.56 (t, 4H, $J=5.5$). ^{13}C-NMR (50 MHz) δ: 3.9, 24.7, 30.0. *Anal.* Calcd for $C_6H_{14}Se_2$: C, 29.52; H, 5.78. Found: C, 29.28; H, 5.51.

A suspension of sodium borohydride (182 mg, 4.8 mmol) and dimethyl diselenide (348 mg, 1.9 mmol) in dry THF (20 ml) was heated for 1.5 h at refluxing temperature. It was cooled to room temperature, then anhydrous aluminum chloride (641 mg, 4.8 mmol) was added. The whole was refluxed again for 30 min, poured into a 10% aqueous HCl solution and extracted with dichloromethane. The extract was washed with brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a residue, which was subjected to silica-gel column chromatography with hexane–ethyl acetate (10 : 1 to 0 : 10) as the eluent, to yield **1** (5.2 mg, 1%) from the less polar fraction, and **2** (405 mg, 65%) from the more polar fraction. **2**: Yellow oil. IR ($CHCl_3$) cm^{-1}: 3450, 2950, 1425, 1230, 1055, 1030. ^{1}H-NMR (500 MHz) δ: 1.65—1.77 (m, 4H), 1.98 (s, 3H), 2.57 (t, 2H, $J=6.8$), 3.66 (t, 2H, $J=6.8$). ^{13}C-NMR (125 MHz) δ: 3.9, 25.1, 26.3, 32.7, 62.1. *Anal.* Calcd for $C_5H_{12}OSe$: C, 35.94; H, 7.24. Found: C, 35.86; H, 6.95.

Substitution Reaction of Primary Benzyl Alcohols (Table 1). General Procedure (Entry 12) A suspension of sodium borohydride (477 mg, 12.6 mmol) and dimethyl diselenide (119 mg, 0.63 mmol) in dry acetonitrile (8 ml) was heated for 1 h under reflux. After the color of the mixture changed from yellow to white, *p*-methylbenzyl alcohol (126 mg, 1.03 mmol) and then anhydrous aluminum chloride (1.37 g, 10.3 mmol) were added portionwise to the mixture at room temperature. The reaction mixture was refluxed again for 4 h, poured into a dilute aqueous HCl solution and extracted with ether. The extract was washed with brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a residue which was subjected to silica-gel column chromatography with hexane to yield **11** (164 mg, 80%).

1-Methyl-4-[(methylseleno)methyl]benzene (**11**)[13]: Yellow oil. IR ($CHCl_3$) cm^{-1}: 3025, 2950, 1520, 820. ^1H-NMR (200 MHz) δ: 1.90 (s, 3H), 2.32 (s, 3H), 3.71 (s, 2H), 7.13 (ABq, 4H, $J=8.0$, $\nu=11.5$). ^{13}C-NMR (125 MHz) δ: 4.2, 21.1, 28.0, 128.6, 129.1, 136.1, 136.2.

[(Phenylseleno)methyl]benzene (**3**)[13—16]: Colorless plates: mp 30.8—31.5 °C (hexane) (lit.[15] mp 31—32 °C). IR ($CHCl_3$) cm^{-1}: 1585, 1505, 1485, 690. ^1H-NMR (500 MHz) δ: 4.11 (s, 2H), 7.20—7.26 (m, 8H), 7.44—7.46 (m, 2H). ^{13}C-NMR (50 MHz) δ: 32.2, 126.8, 127.2, 128.4, 128.9, 130.4, 133.5, 138.6. *Anal.* Calcd for $C_{13}H_{12}Se$: C, 63.16; H, 4.89. Found: C, 62.94; H, 4.91.

1-Methoxy-4-[(phenylseleno)methyl]benzene (**4**)[16,17]: Colorless plates: mp 66—68 °C (Et_2O) (lit.[17] mp 74—75 °C). IR (KBr) cm^{-1}: 1520, 1255, 1040, 835, 730, 690. ^1H-NMR (500 MHz) δ: 3.78 (s, 3H), 4.08 (s, 2H), 6.78 (d, 2H, $J=8.5$), 7.13 (d, 2H, $J=8.5$), 7.24—7.26 (m, 3H), 7.44—7.46 (m, 2H). ^{13}C-NMR (50 MHz) δ: 31.7, 55.2, 113.8, 127.1, 128.9, 129.9, 130.5, 130.6, 133.4, 158.5. *Anal.* Calcd for $C_{14}H_{14}OSe$: C, 60.66; H, 5.09. Found: C, 60.71; H, 5.14.

1-Methoxy-3-[(phenylseleno)methyl]benzene (**5**): Yellow oil. IR ($CHCl_3$) cm^{-1}: 1605, 1595, 1495, 1440, 1265, 1155, 1040, 690. ^1H-NMR (200 MHz) δ: 3.73 (s, 3H), 4.08 (s, 2H), 6.72—6.82 (m, 3H), 7.23—7.26 (m, 4H), 7.44—7.49 (m, 2H). ^{13}C-NMR (125 MHz) δ: 32.2, 55.1, 112.7, 114.0, 121.1, 127.3, 128.9, 129.4, 130.3, 133.5, 140.1, 159.4. FAB-MS (positive ion mode) m/z: 275, 276, 277, 278 (M^+), 279, 280.

1-Chloro-4-[(phenylseleno)methyl]benzene (**6**)[13,17]: Colorless plates: mp 59.5—60.5 °C (hexane–ethyl acetate) (lit.[17] mp 57.5—58.5 °C). IR (KBr) cm^{-1}: 1475, 1090, 720 cm^{-1}. ^1H-NMR (200 MHz) δ: 4.04 (s, 2H), 7.14 (ABq, 4H, $J=8.6$, $\nu=20.5$), 7.21—7.27 (m, 3H), 7.40—7.45 (m, 2H). ^{13}C-NMR (50 MHz) δ: 31.4, 127.6, 128.5, 129.0, 129.7, 130.1, 132.5, 133.9, 137.3. *Anal.* Calcd for $C_{13}H_{11}ClSe$: C, 55.44; H, 3.94. Found: C, 55.74; H, 4.23.

1-Methyl-4-[(phenylseleno)methyl]benzene (**7**)[13,16,17]: Colorless plates: mp <30 °C (Et_2O) (lit.[17] mp 29—31 °C). IR ($CHCl_3$) cm^{-1}: 3030, 1525, 1485, 1445, 1130, 695. ^1H-NMR (200 MHz) δ: 2.31 (s, 3H), 4.09 (s, 2H), 7.08 (ABq, 4H, $J=8.3$, $\nu=9.9$), 7.21—7.27 (m, 3H), 7.43—7.48 (m, 2H). ^{13}C-NMR (50 MHz) δ: 21.1, 31.9, 127.1, 128.7, 128.9, 129.1, 130.7, 133.3, 135.4, 136.5. *Anal.* Calcd for $C_{14}H_{14}Se$: C, 64.37; H, 5.40. Found: C, 64.85; H, 5.61.

[(Methylseleno)methyl]benzene (**8**)[12,13,18]: Yellow oil. IR ($CHCl_3$) cm^{-1}: 2960, 1505, 1460, 695. ^1H-NMR (200 MHz) δ: 1.91 (s, 3H), 3.74 (s, 2H), 7.25—7.30 (m, 5H). ^{13}C-NMR (50 MHz) δ: 4.2, 28.3, 126.6, 128.4, 128.7, 139.2.

1-Methoxy-4-[(methylseleno)methyl]benzene (**9**)[19]: Yellow oil. IR ($CHCl_3$) cm^{-1}: 2960, 1615, 1515, 1250, 1180, 1040, 835. ^1H-NMR (500 MHz) δ: 1.90 (s, 3H), 3.72 (s, 2H), 3.79 (s, 3H), 6.83 (d, 2H, $J=8.5$), 7.20 (d, 2H, $J=8.5$). ^{13}C-NMR (50 MHz) δ: 4.1, 27.7, 55.2, 113.8, 129.8, 131.2, 158.3. *Anal.* Calcd for $C_9H_{12}OSe$: C, 50.24; H, 5.62. Found: C, 50.19; H, 5.53.

1-Chloro-4-[(methylseleno)methyl]benzene (**10**)[13]: Yellow oil. IR ($CHCl_3$) cm^{-1}: 2960, 1500, 1100, 1015, 835. ^1H-NMR (200 MHz) δ: 1.90 (s, 3H), 3.70 (s, 2H), 7.23 (ABq, 4H, $J=8.5$, $\nu=11.0$). ^{13}C-NMR (125 MHz) δ: 4.2, 27.4, 128.5, 130.1, 132.3, 137.8. *Anal.* Calcd for C_8H_9ClSe: C, 43.76; H 4.13. Found: C, 43.81; H, 4.11.

Substitution Reaction of Secondary or Tertiary Alcohols (Table 2). General Procedure (Entry 1) A suspension of sodium borohydride (308 mg, 8.2 mmol) and dimethyl diselenide (77 mg, 0.41 mmol) in dry acetonitrile (5 ml) was heated for 1 h under reflux. After the color of the mixture changed from yellow to white, diphenylmethanol (150 mg, 0.81 mmol) and then anhydrous aluminum chloride (1.09 g, 8.2 mmol) were added portionwise to the mixture at room temperature. The reaction mixture was refluxed again for 3.5 h poured into a 10% aqueous HCl solution and extracted with ether. The extract was washed with brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a residue, which was subjected to silica-gel column chromatography with hexane–ethyl acetate (4 : 1) to yield **12** (153 mg, 72%) and to recover the diphenylmethanol (4.5 mg, 3%).

Diphenylmethyl Methyl Selenide (**12**): Colorless needles: mp 36—39 °C (Et_2O). IR (KBr) cm^{-1}: 3050, 1500, 1455, 700. ^1H-NMR (200 MHz) δ: 1.86 (s, 3H), 5.33 (s, 1H), 7.21—7.35 (m, 6H), 7.42—7.46 (m, 4H). ^{13}C-NMR (50 MHz) δ: 6.3, 48.6, 126.9, 128.5, 128.6, 141.5. *Anal.* Calcd for $C_{14}H_{14}Se$: C, 64.37; H, 5.40. Found: C, 64.39; H, 5.35.

1,2,3,4-Tetrahydro-1-(methylseleno)naphthalene (**13**): Yellow oil. IR ($CHCl_3$) cm^{-1}: 2950, 1455. ^1H-NMR (200 MHz) δ: 1.79—1.85 (m, 1H), 2.00 (s, 3H), 2.11—2.14 (m, 3H), 2.77—2.84 (m, 2H), 4.39 (t, 1H, $J=3.8$), 7.03—7.13 (m, 3H), 7.32—7.37 (m, 1H). ^{13}C-NMR (125 MHz) δ: 5.0, 19.5, 29.0, 29.4, 39.6, 125.6, 126.5, 129.2, 130.2, 136.9, 137.1. *Anal.* Calcd for $C_{11}H_{14}Se$: C, 58.67; H, 6.27. Found: C, 58.27; H, 6.09. FAB-MS (positive ion mode) m/z: 131 $[M-SeMe]^+$.

Methyl Trityl Selenide (**14**)[20]: Colorless prisms: mp 139—140 °C (Et_2O) (lit.[20] mp 131 °C). IR (KBr) cm^{-1}: 3100, 1495, 1445, 755, 735, 695. ^1H-NMR (200 MHz) δ: 1.76 (s, 3H), 7.20—7.38 (m, 15H). ^{13}C-NMR (50 MHz) δ: 8.6, 63.4, 126.5, 127.9, 129.9, 145.5. *Anal.* Calcd for $C_{20}H_{18}Se$: C, 71.21; H, 5.38. Found: C, 71.11; H, 5.51. FAB-MS (positive ion mode) m/z: 243 $[M-SeMe]^+$.

[1-Methyl-1-(methylseleno)ethyl]benzene (**15**)[21]: Yellow oil. IR ($CHCl_3$) cm^{-1}: 3000, 1500, 1130, 1100, 695. ^1H-NMR (200 MHz) δ: 1.75 (s, 3H), 1.84 (s, 6H), 7.15—7.35 (m, 3H), 7.50—7.54 (m, 2H). ^{13}C-NMR (125 MHz) δ: 3.8, 30.3, 42.2, 126.2, 128.0, 146.9. *Anal.* Calcd for $C_{10}H_{14}Se$: C, 56.34; H, 6.62. Found: C, 56.05; H, 6.47.

Reductive Selenation Reaction of Carbonyl Compounds (Table 3). General Procedure (Entry 1) A suspension of sodium borohydride (322 mg, 8.5 mmol) and dimethyl diselenide (80 mg, 0.43 mmol) in dry acetonitrile (5.5 ml) was heated for 1 h under reflux. After the color of the mixture changed from yellow to white, benzaldehyde (92 mg, 0.87 mmol) and then anhydrous aluminum chloride (1.2 g, 8.7 mmol) were added portionwise to the mixture at room temperature. The reaction mixture was refluxed again for 5 h, poured into a 10% aqueous HCl solution and extracted with ether. The extract was washed with brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a residue, which was subjected to a silica-gel column chromatography with hexane–ethyl acetate (10 : 1) to yield **8** (92 mg, 58%) and benzyl alcohol (10 mg, 10%).

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