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Synthesis of *Se*-arylmethyl selenoformates by reaction of aluminum arylmethaneselenolates with formates

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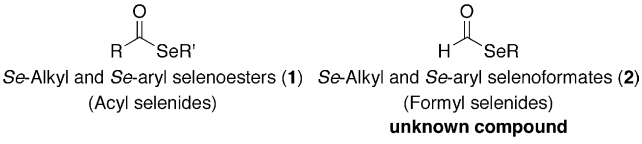
Abstract—*Se*-Arylmethyl selenoformates were synthesized by the reaction of aluminum arylmethaneselenolates with formates. *Se*-Benzyl selenoformate is an unstable compound, but steric protection by some bulky substituents enabled the stable isolation of the selenoformates. To the best of our knowledge, this is the first example of the synthesis of *Se*-alkyl selenoformates.

Se-Alkyl and *Se*-aryl selenoesters (**1**)[1] are synthetically useful compounds as precursors of acyl radicals. The acyl radicals attack unsaturated bonds inter- or intramolecularly to give acyclic and cyclic ketones,[2] or suffer decarbonylation followed by hydrogenation to give reductive products.[3] Hence **1** has been used as intermediates for the synthesis of natural products and for reduction of carbonyl compounds. The synthetic utility of **1** was also demonstrated as a precursor of acyl cations by the reaction with Cu(I), Cu(II), and Hg(II) salts to give various carbonyl compounds.[4] Selenoesters (**1**) can also be easily converted into the corresponding ketones,[5] aldehydes,[6] esters,[7] amides,[7b,8] carboxylic acids,[9] thioesters,[10] selenothioesters,[11] *O*,*Se*-ketene acetals,[12] α-selenoketones,[13] alkenyl selenides,[14] diselenides,[15] heterocyclic compounds,[16] and so on,[17] by various chemical transformations under mild conditions. Due to the versatile synthetic utilities of the selenoesters, the number of hitherto synthesized selenoesters has reached over 1000. On the other hand, to the best of our knowledge, *Se*-alkyl and *Se*-aryl selenoformates (**2**), namely, the formyl selenides, are still unknown compounds, although **2** has the possibility to become an excellent precursor of formyl radical and formyl cation (Scheme 1).[18,19] We now report the first synthesis of **2** by the reaction of aluminum selenolates with formates.



Scheme 1.

Se-Alkyl and *Se*-aryl selenoesters have been generally prepared by the acylation of selenols and their salts.[1,20] As one of the alternative method for the synthesis of selenoesters, Kozikowski et al. developed the reaction of aluminum selenolate with esters.[4a,c,d,5a,b,21] On the other hand, *S*-alkyl and *S*-aryl thioformates, that is, an analogue of the selenoformates, are known to be synthesized by (i) the formylation of thiols[22] and disulfides,[23] (ii) the hydrolysis of *ortho*thioesters,[24] (iii) the reduction of chlorothioformates,[25] (iv) the ozonolysis of alkenyl sulfides,[26] (v) the acid-catalyzed hydrolysis of thioformimidates,[27] (vi) the reaction of aluminum sulfides with formates,[28] and (vii) the thermolysis of 3-phenylthio-1,2-dioxetanes.[29] For the synthesis of selenoformates with readily available and easily handled formylating reagents, we carried out the reaction of aluminum selenolate with alkyl and aryl formates.

We first attempted the synthesis of *Se*-benzyl selenoformate (**2a**) (Eq. 1). Aluminum phenylmethaneselenolate was prepared by the reaction of dibenzyl diselenide (**3a**)[30] with *i*-Bu_2AlH (1.0 M in hexane) at 20 °C for 1 h.[31] The solution was then allowed to react with propyl formate (**4a**). The addition of water and

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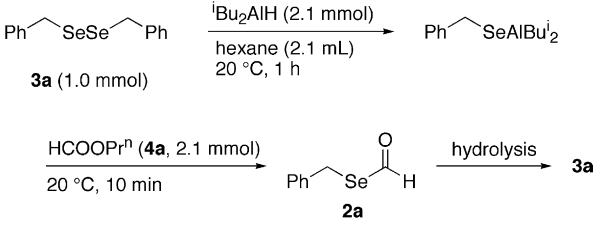
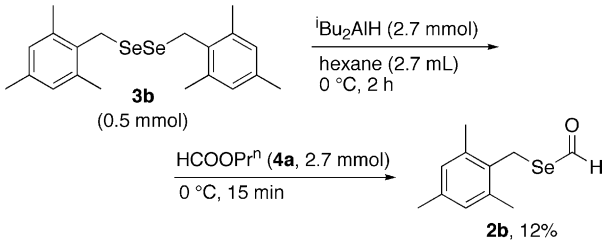
extraction with Et_2O gave a crude mixture containing **2a**. Purification by recycling preparative HPLC (eluent: $CHCl_3$) gave pure **2a** as a yellow oil in 7% isolated yield, but it gradually decomposed to the starting dibenzyl diselenide (**3a**) when the isolated product was left in aerated conditions at room temperature. Column chromatography on silica gel also caused the decomposition of **2a** to **3a**. Compound **2a** might be susceptible to hydrolysis due to the excellent leaving ability of the alkylseleno group.



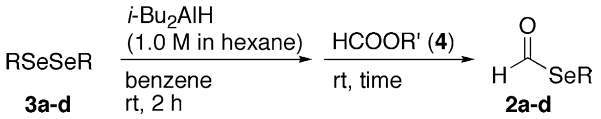
(1)

The instability of **2a** let us examine the steric protection of the selenoformate. When aluminum selenolate generated from bis(2,4,6-trimethylphenylmethyl) diselenide (**3b**) and *i*-Bu_2AlH was allowed to react with propyl formate under conditions similar to those described above at 0 °C, *Se*-2,4,6-trimethylphenylmethyl selenoformate (**2b**) could be isolated by recycling preparative HPLC in 12% isolated yield (Eq. 2). Selenoformate **2b** was a stable yellow solid and it was not decomposed after several months by storage in an argon-purged flask in a refrigerator. To the best of our knowledge, this is the first example of the synthesis of stable *Se*-alkyl selenoformates.



(2)

We have now investigated the optimization of the reaction conditions and the results are summarized in Eq. 3 and Table 1. Entries 1 and 2 correspond to the results shown in Eqs. 1 and 2. When the 2,4,6-triisopropylphenyl group was employed as a more bulky substituent, *Se*-2,4,6-triisopropylphenylmethyl selenoformate (**2c**) was obtained in 18% yield (entry 3). Methyl formate (**4b**) can also be used for the synthesis of **2c** (entry 4). The yield of selenoformate **2c** increased to 42% when phenyl formate (**4c**) was used as the formylating reagent (entry 5).[32] The yields of the selenoformates were changed by the equivalents of *i*-Bu_2AlH and **4**. The use of excess amounts of *i*-Bu_2AlH and **4** gave better yields (compare entries 5 and 6). The yields of the selenoformates were also affected by the reaction time with **4** before quenching by water (compare entries 5, 7, and 8). A similar reaction using bis(9-anthrylmethyl) diselenide (**3d**) gave *Se*-9-anthrylmethyl selenoformate (**2d**) in 26% yield.



a: R = $PhCH_2$ **b**: R = 2,4,6-$Me_3C_6H_2CH_2$
c: R = 2,4,6-(*i*-Pr)$_3C_6H_2CH_2$ **d**: R = 9-anthrylmethyl

(3)

Table 1. Synthesis of *Se*-arylmethyl selenoformates

Entry	3	4	Equivalents of *i*-Bu_2AlH and **4**	Time (min)[a]	2	Yield of 2[b] (%)
1[c]	**3a**	**4a** (R′ = *n*-Pr)	2	10	**2a**	7
2[c,d]	**3b**	**4a**	5	15	**2b**	12
3	**3c**	**4a**	5	20	**2c**	18
4	**3c**	**4b** (R′ = Me)	5	20	**2c**	21
5	**3c**	**4c** (R′ = Ph)	5	20	**2c**	42
6	**3c**	**4c**	2	20	**2c**	25
7	**3c**	**4c**	5	3	**2c**	31
8	**3c**	**4c**	5	60	**2c**	11
9	**3d**	**4c**	5	20	**2d**	26

[a] Reaction time with **4**.
[b] Isolated yield.
[c] Without benzene.
[d] Cooled by an ice bath.

These successful results are attributable to the affinity between aluminum and oxygen. Benzene was added in entries 3–9 to increase the solubility of **3**. In all the entries, other products were concomitantly produced, but their structures could not be determined. It is unclear why the longer reaction time of aluminum selenolate with formates before quenching by water resulted in the decrease of the yield.[33] Although 2 equiv of *i*-Bu_2AlH based on diselenides satisfy the stoichiometry of the reaction, the addition of excess of *i*-Bu_2AlH rather gave better yields of **2**. *i*-Bu_2AlH may also act as a Lewis acid coordinated on the carbonyl oxygen. When diphenyl diselenide was used, a very poor yield of *Se*-phenyl selenoformate was formed, and most of diphenyl diselenide was recovered. Since PhSeAlBu-i_2 must be produced under the present reaction conditions,[31] the result can be explained by the low nucleophilicity and good leaving ability of $PhSe^-$ compared with those of $ArCH_2Se^-$.

The spectral data of the selenoformates **2a–d** are in good agreement with their structures.[34] Some spectral data of these new compounds and related compounds are summarized in Table 2. In the ^1H and ^{13}C NMR spectra, the formyl hydrogens of the selenoformates appeared at about 11.6 ppm, and carbonyl carbons appeared at about 191 ppm. These are downfield shifted signals compared with those of *S*-benzyl thioformate (**5**)[22f] and benzyl formate (**6**).[35] The IR absorption bands of the CO double bonds appeared in a similar region (1658–1676 cm^{-1}) with the thioformates.

In conclusion, we synthesized unprecedented *Se*-alkyl selenoformates by the reaction of aluminum selenolates with formates. Although the *Se*-benzyl selenoformate

Table 2. Spectral data of *Se*-arylmethyl selenoformates and related compounds

Compound	^{1}H NMR (CHO, ppm)	^{13}C NMR (C=O, ppm)	IR (C=O, cm^{-1})
$PhCH_2SeC(O)H$ (**2a**)	11.56[a]	190.42[b]	1674[c]
2,4,6-$Me_3C_6H_2CH_2SeC(O)H$ (**2b**)	11.60[d]	191.38[e]	1667[f]
2,4,6-$^i Pr_3C_6H_2CH_2SeC(O)H$ (**2c**)	11.60[d]	191.47[e]	1676[f]
9-Anthryl-$CH_2SeC(O)H$ (**2d**)	11.68[d]	190.80[e]	1658[f]
$PhCH_2SC(O)H$ (**5**)	10.15[g,h]	186.58[i,h]	1666[c,h]
$PhCH_2OC(O)H$ (**6**)	8.05[d,j]	160.7[e,j]	1724[c,j]

[a] 270 MHz, $CDCl_3$.
[b] 68 MHz, $CDCl_3$.
[c] Neat.
[d] 300 MHz, $CDCl_3$.
[e] 75 MHz, $CDCl_3$.
[f] KBr.
[g] 200 MHz, $CDCl_3$.
[h] Data from Ref. 22f.
[i] 50 MHz, $CDCl_3$.
[j] Data from Ref. 35.

(**2a**) gradually decomposed to dibenzyl diselenide, the 2,4,6-trimethylphenylmethyl, 2,4,6-triisopropylphenylmethyl, and anthrylmethyl selenoformates could be isolated as stable compounds. Synthetic utilization of the selenoformates are now under investigation.

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References and notes

1. (a) Ogawa, A.; Sonoda, N. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 6, pp 461–484; (b) Ogawa, A.; Sonoda, N. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon: Oxford, 1995; Vol. 5, pp 231–255.
2. (a) Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1988**, *53*, 3377–3379; (b) Bachi, M. D.; Denenmark, D. *Heterocycles* **1989**, *28*, 583–588; (c) Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1989**, *54*, 1777–1779; (d) Crich, D.; Eustace, K. A.; Fortt, S. M.; Ritchie, T. J. *Tetrahedron* **1990**, *46*, 2135–2148; (e) Boger, D. L.; Mathvink, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 4003–4008; (f) Boger, D. L.; Mathvink, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 4008–4011; (g) Astley, M. P.; Pattenden, G. *Synlett* **1991**, 335–336; (h) Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1992**, *57*, 1429–1443; (i) Batty, D.; Crich, D. *J. Chem. Soc., Perkin Trans. 1* **1992**, 3193–3204; (j) Chen, L.; Gill, G. B.; Pattenden, G. *Tetrahedron Lett.* **1994**, *35*, 2593–2596; (k) Evans, P. A.; Roseman, J. D. *Tetrahedron Lett.* **1995**, *36*, 31–34; (l) Batsanov, A.; Chen, L.; Gill, G. B.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1* **1996**, 45–55; (m) Hayes, C. J.; Pattenden, G. *Tetrahedron Lett.* **1996**, *37*, 271–274; (n) Kim, S.; Jon, S. Y. *Chem. Commun.* **1996**, 1335–1336; (o) Evans, P. A.; Roseman, J. D. *J. Org. Chem.* **1996**, *61*, 2252–2253; (p) Herbert, N.; Pattenden, G. *Synlett* **1997**, 69–70; (q) Chatgilialoglu, C.; Ferreri, C.; Lucarini, M.; Venturini, A.; Zavitsas, A. A. *Chem. Eur. J.* **1997**, *3*, 376–387; (r) Pattenden, G.; Roberts, L.; Blake, A. J. *J. Chem. Soc., Perkin Trans. 1* **1998**, 863–868; (s) Handa, S.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1* **1999**, 843–845; (t) Harrington-Frost, N. M.; Pattenden, G. *Synlett* **1999**, 1917–1918; (u) Handa, S.; Nair, P. S.; Pattenden, G. *Helv. Chim. Acta* **2000**, *83*, 2629–2643; (v) Boehm, H. M.; Handa, S.; Pattenden, G.; Roberts, L.; Blake, A. J.; Li, W.-S. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3522–3538; (w) Evans, P. A.; Manangan, T. *J. Org. Chem.* **2000**, *65*, 4523–4528; (x) Evans, P. A.; Manangan, T.; Rheingold, A. L. *J. Am. Chem. Soc.* **2000**, *122*, 11009–11010; (y) Ollivier, C.; Panchaud, P.; Renaud, P. *Synthesis* **2001**, 1573–1578; (z) Bennasar, M.-L.; Roca, T.; Griera, R.; Bosch, J. *Org. Lett.* **2001**, *3*, 1697–1700; (aa) Bennasar, M.-L.; Roca, T.; Griera, R.; Bosch, J. *J. Org. Chem.* **2001**, *66*, 7547–7551; (bb) Allin, S. M.; Barton, W. R. S.; Bowman, W. R.; McInally, T. *Tetrahedron Lett.* **2001**, *42*, 7887–7890; (cc) Bennasar, M.-L.; Roca, T.; Griera, R.; Bassa, M.; Bosch, J. *J. Org. Chem.* **2002**, *67*, 6268–6271.
3. (a) Ireland, R. E.; Norbeck, D. W.; Mandel, G. S.; Mandel, N. S. *J. Am. Chem. Soc.* **1985**, *107*, 3285–3294; (b) Ireland, R. E.; Varney, M. D. *J. Org. Chem.* **1986**, *51*, 635–648; (c) Smith, A. L.; Williams, S. F.; Holmes, A. B.; Hughes, L. R.; Lidert, Z.; Swithenbank, C. *J. Am. Chem. Soc.* **1988**, *110*, 8696–8698; (d) Holmes, A. B.; Smith, A. L.; Williams, S. F.; Hughes, L. R.; Lidert, Z.; Swithenbank, C. *J. Org. Chem.* **1991**, *56*, 1393–1405; (e) Stoilov, I.; Kolaczkowska, E.; Watt, D. S.; Pyrek, J. St.; Carlson, R. M. K.; Fago, F. J.; Moldowan, J. M. *J. Org. Chem.* **1993**, *58*, 3444–3454; (f) Giese, B.; Erdmann, P.; Giraud, L.; Göbel, T.; Petretta, M.; Schäfer, T.; Raumer, M. *Tetrahedron Lett.* **1994**, *35*, 2683–2686; (g) Chatgilialoglu, C.; Ferreri, C.; Lucarini, M.; Pedrielli, P.; Pedulli, G. F. *Organometallics* **1995**, *14*, 2672–2676; (h) Wipf, P.; Kim, Y.; Goldstein, D. M. *J. Am. Chem. Soc.* **1995**, *117*, 11106–11112; (i) Stojanovic, A.; Renaud, P. *Synlett* **1997**, 181–182; (j) Alcaide, B.; Rodríguez-Vicente, A.; Sierra, M. A. *Tetrahedron Lett.* **1998**, *39*, 163–166; (k) Stojanovic, A.; Renaud, P.; Schenk, K. *Helv. Chim. Acta* **1998**, *81*, 268–284; (l) Deiters, A.; Chen, K.; Eary, C. T.; Martin, S. F. *J. Am. Chem. Soc.* **2003**, *125*, 4541–4550.
4. (a) Kozikowski, A. P.; Ames, A. *J. Org. Chem.* **1978**, *43*, 2735–2737; (b) Kozikowski, A. P.; Ames, A. *J. Am. Chem. Soc.* **1980**, *102*, 860–862; (c) Kozikowski, A. P.; Ames, A. *Tetrahedron* **1985**, *41*, 4821–4834; (d) Subramanyam, C.; Noguchi, M.; Weinreb, S. M. *J. Org. Chem.* **1989**, *54*, 5580–5585; (e) Dabdoub, M. J.; Viana, L. H. *Synth. Commun.* **1992**, *22*, 1619–1625; (f) Hawker, C. J.; Petersen, P. M.; Leeper, F. J.; Battersby, A. R. *J. Chem. Soc.,*

Perkin Trans. 1 **1998**, 1519–1530; (g) Campiani, G.; Nacci, V.; Bechelli, S.; Ciani, S. M.; Garofalo, A.; Fiorini, I.; Wikström, H.; de Boer, P.; Liao, Y.; Tepper, P. G.; Cagnotto, A.; Mennini, T. *J. Med. Chem.* **1998**, *41*, 3763–3772.

5. (a) Sviridov, A. F.; Ermolenko, M. S.; Yashunsky, D. V.; Kochetkov, N. K. *Tetrahedron Lett.* **1983**, *24*, 4355–4358; (b) Sviridov, A. F.; Ermolenko, M. S.; Yashunsky, D. V.; Kochetkov, N. K. *Tetrahedron Lett.* **1983**, *24*, 4359–4362.
6. Kuniyasu, H.; Ogawa, A.; Higaki, K.; Sonoda, N. *Organometallics* **1992**, *11*, 3937–3939.
7. (a) Mattia, K. M.; Ganem, B. *J. Org. Chem.* **1994**, *59*, 720–728; (b) Tiecco, M.; Testaferri, L.; Temperini, A.; Bagnoli, L.; Marini, F.; Santi, C.; Terlizzi, R. *Eur. J. Org. Chem.* **2004**, 3447–3458.
8. (a) Mautner, H. G.; Günther, W. H. H. *J. Am. Chem. Soc.* **1961**, *83*, 3342–3343; (b) Mautner, H. G.; Chu, S.-H.; Günther, W. H. H. *J. Am. Chem. Soc.* **1963**, *85*, 3458–3462; (c) Günther, W. H. H. *J. Org. Chem.* **1966**, *31*, 1202–1205; (d) Günther, W. H. H. *J. Org. Chem.* **1967**, *32*, 3929–3931; (e) Jacquemin, P. V.; Christiaens, L. E.; Renson, M. J.; Evers, M. J.; Dereu, N.; Rorer, R.-P. *Tetrahedron Lett.* **1992**, *33*, 3863–3866.
9. (a) Gosselck, J.; Barth, H.; Béress, L. *Justus Liebigs Ann. Chem.* **1964**, *671*, 1–9; (b) Gosselck, J. *Angew. Chem.* **1963**, *75*, 831–840; (c) Zeltner, S.; Olk, R.-M.; Wagner, M.; Olk, B. *Synthesis* **1994**, 1445–1449; (d) Wagner, M.; Madsen, D.; Markussen, J.; Larsen, S.; Schaumburg, K.; Lubert, K.-H.; Becher, J.; Olk, R.-M. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1995–1998.
10. Makriyannis, A.; Günther, W. H. H.; Mautner, H. G. *J. Am. Chem. Soc.* **1973**, *95*, 8403–8406.
11. (a) Kato, S.; Komuro, T.; Kanda, T.; Ishihara, H.; Murai, T. *J. Am. Chem. Soc.* **1993**, *115*, 3000–3001; (b) Murai, T.; Kakami, K.; Hayashi, A.; Komuro, T.; Takada, H.; Fujii, M.; Kanda, T.; Kato, S. *J. Am. Chem. Soc.* **1997**, *119*, 8592–8597.
12. Abe, M.; Tachibana, K.; Fujimoto, K.; Nojima, M. *Synthesis* **2001**, 1243–1247.
13. (a) Back, T. G.; Kerr, R. G. *Tetrahedron Lett.* **1982**, *23*, 3241–3244; (b) Back, T. G.; Kerr, R. G. *Tetrahedron* **1985**, *41*, 4759–4764.
14. (a) Takahashi, K.; Tomitani, K.; Ise, T.; Shirahata, T. *Chem. Lett.* **1995**, 619–620; (b) Petasis, N. A.; Lu, S.-P. *Tetrahedron Lett.* **1995**, *36*, 2393–2396; (c) Takahashi, K.; Ise, T.; Mori, T.; Mori, H.; Tanaka, S. *Chem. Lett.* **1996**, 1001–1002; (d) Zhao, C.-Q.; Huang, X. *Synth. Commun.* **1996**, *26*, 3607–3611; (e) Takahashi, K.; Ise, T. *Heterocycles* **1997**, *45*, 1051–1054; (f) Huang, X.; Zhao, C.-Q. *Synth. Commun.* **1997**, *27*, 3491–3495; (g) Koketsu, M.; Miyajima, Y.; Ishihara, H. *Chem. Lett.* **1998**, 645–646; (h) Zhao, C.-Q.; Huang, X.; Meng, J.-B. *Tetrahedron Lett* **1998**, *39*, 1933–1936; (i) Hirai, T.; Kuniyasu, H.; Kato, T.; Kurata, Y.; Kambe, N. *Org. Lett.* **2003**, *5*, 3871–3873.
15. (a) Roy, J.; Gordon, W.; Schwartz, I. L.; Walter, R. *J. Org. Chem.* **1970**, *35*, 510–513; (b) Wenkert, E.; Chianelli, D. *J. Chem. Soc., Chem. Commun.* **1991**, 627–628; (c) Mohsine, A.; Christiaens, L. *Heterocycles* **1996**, *43*, 2567–2593; (d) Reinerth, W. A.; Tour, J. M. *J. Org. Chem.* **1998**, *63*, 2397–2400.
16. (a) Pakzad, B.; Praefcke, K.; Simon, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 319–320; (b) Lüdersdorf, R.; Martens, J.; Pakzad, B.; Praefcke, K. *Liebigs Ann. Chem.* **1977**, 1992–2017; (c) Praefcke, K.; Schmidt, D. *J. Heterocycl. Chem.* **1979**, *16*, 47–48; (d) Paulmier, C. *Bull. Soc. Chim. Fr., Part 2* **1980**, 151–156; (e) Praefcke, K.; Schulze, U. *J. Organomet. Chem.* **1980**, *184*, 189–193.
17. (a) Testaferri, L.; Tiecco, M.; Tingoli, M.; Chianelli, D. *Tetrahedron* **1986**, *42*, 63–69; (b) Testaferri, L.; Tiecco, M.; Tingoli, M.; Chianelli, D. *Tetrahedron* **1986**, *42*, 4577–4584; (c) Byeon, C.-H.; Hart, D. J.; Lai, C.-S.; Unch, J. *Synlett* **2000**, 119–121.
18. *O*-Alkyl and *O*-aryl selenoformates are known compounds (a) Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc. Perkin Trans. 1* **1975**, 1574–1585; (b) Forrest, D.; Ingold, K. U.; Barton, D. H. R. *J. Phys. Chem.* **1977**, *81*, 915–918; (c) Barton, D. H. R.; Hansen, P.-E.; Picker, K. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1723–1730; (d) Okazaki, R.; Ishii, A.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1986**, 71–72; (e) Ishii, A.; Okazaki, R.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2529–2535; (f) Ishii, A.; Okazaki, R.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1037–1040.
19. It is ambiguous that compounds RSeC(O)OR′ are also called selenoformates (a) Lucas, M. A.; Schiesser, C. H. *J. Org. Chem.* **1996**, *61*, 5754–5761; (b) Schiesser, C. H.; Skidmore, M. A. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2689–2690; (c) Wang, L.; Zhang, Y. *Heteroatom Chem.* **1999**, *10*, 203–208; (d) Wang, L.; Zhang, Y. *Synth. Commun.* **1999**, *29*, 3107–3115.
20. Gais, H.-J. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 244–246.
21. (a) Kozikowski, A. P.; Tückmantel, W.; Reynolds, I. J.; Wroblewski, J. T. *J. Med. Chem.* **1990**, *33*, 1561–1571; (b) Schwartz, C. E.; Curran, D. P. *J. Am. Chem. Soc.* **1990**, *112*, 9272–9284; (c) Khalid, M.; Ripoll, J.-L.; Vallée, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 964–965; (d) Lemarié, M.; Vallée, Y.; Worrell, M. *Tetrahedron Lett.* **1992**, *33*, 6131–6134; (e) Murai, T.; Mizutani, T.; Kanda, T.; Kato, S. *J. Am. Chem. Soc.* **1993**, *115*, 5823–5824; (f) Quirante, J.; Escolano, C.; Bonjoch, J. *Synlett* **1997**, 179–180; (g) Quirante, J.; Vila, X.; Escolano, C.; Bonjoch, J. *J. Org. Chem.* **2002**, *67*, 2323–2328.
22. (a) Olah, G. A.; Kuhn, S. J. *J. Am. Chem. Soc.* **1960**, *82*, 2380–2382; (b) Bax, P. C.; Stevens, W. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 265–269; (c) Dousse, M. M. G.; Satgé, J. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 221–233; (d) Bax, P. C.; Holsboer, D. H.; van der Veek, A. P. M. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 562–567; (e) Yoneda, F.; Higuchi, M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1336–1339; (f) Sprecher, M.; Nov, E. *Synth. Commun.* **1992**, *22*, 2949–2954.
23. Osborne, N. F.; Broom, N. J. P.; Coulton, S.; Harbridge, J. B.; Harris, M. A.; Stirling-Francois, I.; Walker, G. *J. Chem. Soc., Chem. Commun.* **1989**, 371–373.
24. (a) Smith, R. A. J.; Keng, G. S. *Tetrahedron Lett.* **1978**, 675–678; (b) Kruse, C. G.; Wijsman, A.; van der Gen, A. *J. Org. Chem.* **1979**, *44*, 1847–1851; (c) Stahl, I. *Chem. Ber.* **1985**, *118*, 1798–1808.
25. Corriu, R. J. P.; Lanneau, G. F.; Perrot, M. *Tetrahedron Lett.* **1988**, *29*, 1271–1274.
26. Kametani, T.; Chu, S.-D.; Itoh, A.; Wang, T.-C.; Nakayama, A.; Honda, T. *J. Chem. Soc., Chem. Commun.* **1988**, 544–546.
27. Matsubara, Y.; Nakamura, T.; Yoshihara, M.; Maeshima, T. *Chem. Pharm. Bull.* **1982**, *30*, 3389–3391.
28. Hirabayashi, T.; Imaeda, H.; Itoh, K.; Ishii, Y. *J. Organomet. Chem.* **1972**, *42*, 33–40.
29. Adam, W.; Arias, L. A.; Scheutzow, D. *Tetrahedron Lett.* **1982**, *23*, 2835–2836.
30. The bis(arylmethyl) diselenides were prepared by the reaction of arylmethyl chlorides with Na_2Se_2: Klayman, D. L.; Griffin, T. S. *J. Am. Chem. Soc.* **1973**, *95*, 197–199; 2,4,6-Triisopropylphenylmethyl chloride and 2,4,6-trimethylphenylmethyl chloride were prepared by chloromethylation of 2,4,6-triisopropylbenzene and 2,4,6-

trimethylbenzene: Fuson, R. C.; McKeever, C. H. *Org. React.* **1942**, *1*, 63–90.
31. For the preparation of aluminum selenolates by the reaction of diselenides with *i*-Bu_2AlH: (a) Maruoka, K.; Miyazaki, T.; Ando, M.; Matsumura, Y.; Sakane, S.; Hattori, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1983**, *105*, 2831–2843; (b) Bartlett, P. A.; Chouinard, P. M. *J. Org. Chem.* **1983**, *48*, 3854–3855; (c) Inoue, T.; Takeda, T.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *J. Org. Chem.* **1994**, *59*, 5824–5827.
32. To a stirred solution of bis(2,4,6-triisopropylphenylmethyl) diselenide (**3c**, 100 mg, 0.17 mmol) in anhydrous benzene (15 mL) was added *i*-Bu_2AlH (0.95 M in hexane, 0.9 mL, 0.86 mmol) in a water bath to maintain the reaction at room temperature. After stirring the solution for 2 h, phenyl formate (104 mg, 0.85 mmol) was added, and the stirring was continued for 20 min. Then aqueous NH_4Cl solution was added, and the product was extracted from benzene, dried over Na_2SO_4, and concentrated. Purification of the yellow residue by recycling preparative HPLC (GPC, eluent: $CHCl_3$) gave *Se*-2,4,6-triisopropylphenylmethyl selenoformate (**2c**, 46 mg, 42%).
33. It is uncertain whether the tetrahedral intermediate $ArCH_2SeCH(OR)OAlBu\text{-}i_2$ collapsed before or after the addition of water. Some further reaction from the intermediate or selenoformate may occur.
34. *Data for compound* **2a**: ^1H NMR (270 MHz, $CDCl_3$) δ 4.27 (s, 2H), 7.21–7.31 (m, 5H), 11.56 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 26.62, 127.24, 128.73, 128.96, 138.25, 190.42; IR (NaCl) 1674, 1494, 1453, 1323, 697, 648 cm^{-1}; MS (CI) *m*/*z* (%) = 91 (100), 172 (2), 201 (M^++1, 10); HRMS (CI) calcd for C_8H_8OSe: 200.9818. Found: 200.9819. *Data for compound* **2b**: mp 47 °C (dec); ^1H NMR (300 MHz, $CDCl_3$) δ 2.18 (s, 6H), 2.30 (s, 3H), 4.33 (s, 2H), 6.84 (s, 2H), 11.60 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.99, 128.99, 129.95, 136.77, 136.91, 191.38; IR (KBr) 2962, 1667, 1317, 1261, 1029, 802, 651 cm^{-1}; MS (EI) *m*/*z* (%) = 133 (100), 213 (1), 242 (M^+, 2); HRMS (EI) Calcd for $C_{11}H_{14}OSe$: 242.0209. Found: 242.0204. *Data for compound* **2c**: mp 26 °C (dec); ^1H NMR (300 MHz, $CDCl_3$) δ 1.24 (d, J = 6.96 Hz, 6H), 1.25 (d, J = 6.95 Hz, 12H), 2.86 (sept, J = 6.96 Hz, 1H), 3.12 (sept, J = 6.78 Hz, 2H), 4.41 (s, 2H), 6.98 (s, 2H), 11.60 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.66, 24.03, 24.34, 29.64, 34.26, 121.19, 126.95, 147.42, 148.08, 191.47; IR (NaCl) 2961, 1675, 1459, 1320, 647 cm^{-1}; MS (EI), *m*/*z* (%) = 133 (13), 217 (100), 255 (2), 326 (M^+, 1); HRMS (EI) calcd for $C_{17}H_{26}OSe$: 326.1148. Found: 326.1143. *Data for compound* **2d**: mp 119 °C (dec); ^1H NMR (300 MHz, $CDCl_3$) δ 5.34 (s, 2H), 7.47–7.61 (m, 4H), 8.02 (d, J = 8.61 Hz, 2H), 8.20 (d, J = 8.97 Hz, 2H), 8.43 (s, 1H), 11.68 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.76, 123.56, 125.11, 126.39, 127.68, 128.06, 129.23, 129.66, 131.34, 198.80; IR (KBr) 1658, 1623, 1440, 1327, 890, 734, 637 cm^{-1}; MS (EI), *m*/*z* (%) = 191 (100), 300 (M^+, 3); HRMS (EI) Calcd for $C_{16}H_{12}OSe$: 300.0054. Found: 300.0061.
35. Suri, S. C.; Rodgers, S. L.; Radhakrishnan, K. V.; Nair, V. *Synth. Commun.* **1996**, *26*, 1031–1039.