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Reactions of 2,4,6-Tri-*t*-butylphenyllithium with *O*-Alkyl Selenoformates: Intermediate Formation of 2,4,6-Tri-*t*-butylselenobenzaldehyde

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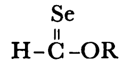
2,4,6-Tri-*t*-butylphenyllithium reacts with *O*-alkyl selenoformates (**1**) at three different sites (i. e., the selenoformyl carbon, the selenoformyl hydrogen, and the selenium) to give 1,3,5-tri-*t*-butylbenzene, 2,4,6-tri-*t*-butylbenzaldehyde, 6,8-di-*t*-butyl-3,4-dihydro-4,4-dimethyl-1*H*-2-benzoselenin(**11**), bis(2,4,6-tri-*t*-butylphenylmethyl) di(and tri) selenides, bis(2,4,6-tri-*t*-butylphenyl) diselenide, and dibutyl diselenide depending on the reaction conditions and the alkyl group in **1**. The formation of **11** is explained in terms of the intermediacy of 2,4,6-tri-*t*-butylselenobenzaldehyde, which is trapped by condensation reaction with butylamine leading to *N*-(2,4,6-tri-*t*-butylbenzylidene)butylamine. Mechanism for the formation of these products is also discussed.

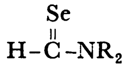
Recently much attention has been paid to the chemistry of the compounds having a multiple bond containing the third or fourth period elements. Among them are the selenocarbonyl compounds. Although sterically crowded selenoketones have been recently synthesized,[1] only a few have been reported for the selenoformyl compound. For example, selenoformaldehyde was generated by flash pyrolysis and characterized by photoelectron spectroscopy,[2] absorption,[3] or phosphorescence spectrum.[4] Selenoacetaldehyde was also characterized by microwave spectrum.[5] However, these selenoaldehydes are extremely unstable and can not exist in the monomeric form under normal conditions,[6] though selenoformaldehyde[7a] and selenobenzaldehyde[7b] have been reported to be stabilized by complexation with transition metals.

There have been isolated the compounds owning a selenoformyl group such as selenoformates **1**,[8] selenoformamide **2**,[9] and their vinylogs like indolizine-1-carboselenaldehyde **3**.[10] The selenoformyl group in these compounds, however, is stabilized by the mesomeric effect due to the lone-pair electrons on heteroatom.



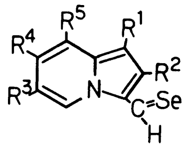
$\mathrm{H\text{-}\overset{\overset{Se}{\|}}{C}\text{-}OR}$

1



$\mathrm{H\text{-}\overset{\overset{Se}{\|}}{C}\text{-}NR_2}$

2



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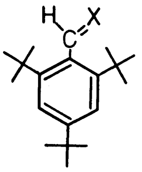
Although the thioaldehyde had also been known too unstable to be isolated, we recently reported the synthesis of 2,4,6-tri-*t*-butylthiobenzaldehyde (**4**) by reaction of 2,4,6-tri-*t*-butylphenyllithium (**5**) with *O*-ethyl thioformate.[11] Compound **4** was the first stable thioaldehyde without above-mentioned electronic stabilization by heteroatoms. In **4**, the highly reactive thioformyl group is protected by two bulky *o*-*t*-butyl groups from oligomerization and from attack by other reagents.

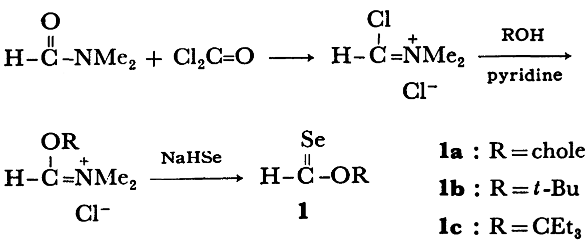
We undertook an investigation on the reaction of **5** with *O*-alkyl selenoformates **1** in the hope that it would also give stable 2,4,6-tri-*t*-butylselenobenzaldehyde (**6**).[12]



4 : X = S
6 : X = Se

Results and Discussion

Synthesis of Selenoformates. *O*-Cholesteryl (**1a**), *O*-*t*-butyl (**1b**),and *O*-(1,1-diethylpropyl) selenoformates (**1c**) were prepared by the Barton's method (Eq. 1)[8] in 70, 22, and 6.5% yields, respectively, the latter two being new compounds.



$$\mathrm{H\text{-}\overset{\overset{O}{\|}}{C}\text{-}NMe_2} + \mathrm{Cl_2C{=}O} \longrightarrow \mathrm{H\text{-}\overset{\overset{Cl}{|}}{C}{=}\overset{+}{N}Me_2\ Cl^-} \xrightarrow[\text{pyridine}]{\text{ROH}} \mathrm{H\text{-}\overset{\overset{OR}{|}}{C}{=}\overset{+}{N}Me_2\ Cl^-} \xrightarrow{\text{NaHSe}} \underset{\mathbf{1}}{\mathrm{H\text{-}\overset{\overset{Se}{\|}}{C}\text{-}OR}} \qquad (1)$$

1a : R = cholesteryl
1b : R = *t*-Bu
1c : R = $\mathrm{CEt_3}$

We also tried to prepare selenoformates derived from primary alcohols (**1d**: R=ethyl; **1e**: R=2,2-dimethylpropyl). Although they existed in a reaction solution, as judged from the presence of characteristic ^{1}H NMR signals due to the selenoformyl proton at ca. δ 12 (cf., δ 12.07, 12.20, and 12.14 for **1a**, **1b**, and **1c**, respectively), they polymerized during concentration to give orange and pale orange jelly for **1d** and **1e**, respectively. The former jellied material was insoluble in organic solvents, while the latter was slightly soluble and showed a small peak due to the selenoformyl group.

The synthesis of *O*-aryl selenoformates (**1f**: R=phenyl; **1g**: R=*p*-methoxyphenyl) was also attempted, but only *N*,*N*-dimethylselenoformamide was obtained in 85 and 74% yields, respectively.

Reactions of Selenoformates 1 with 2,4,6-Tri-*t*-butylphenyllithium (ArLi, 5).[†] A tetrahydrofuran (THF) solution of **1** was added dropwise to **5**, prepared from

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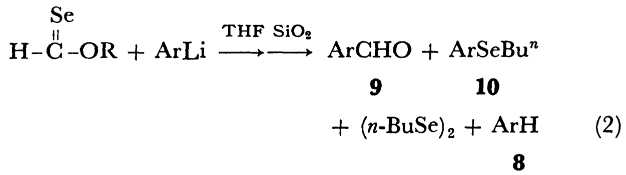
[†] Throughout this paper, Ar denotes 2,4,6-tri-*t*-butylphenyl.

Table 1. Reaction Products of **1a** and **1b** with **5** Prepared from **7** and Butyllithium

R	Yield/%			
	9	**10**	(n-BuSe)$_2$	**8**
Cholesteryl (**1a**)	48	4.5	62	29
t-Butyl (**1b**)	45	15	55	18

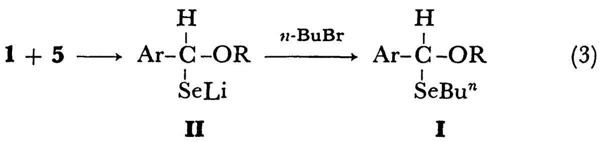
1-bromo-2,4,6-tri-t-butylbenzene (**7**) and butyllithium in THF at −78 °C, and then the reaction mixture was warmed to room temperature. The ^{1}H NMR spectrum of the reaction mixture showed the formation of 1,3,5-tri-t-butylbenzene (**8**) and a small amount of 2,4,6-tri-t-butylbenzaldehyde (**9**). ^{77}Se NMR spectra of the mixture gave signals at δ 360 and 364 for **1a** and δ 442 for **1b**. Appearance of these signals in the region of chemical shifts of selenides suggested the existence of relatively stable selenides in the crude reaction mixture. Chromatography of the reaction mixture on silica gel gave aldehyde **9**, butyl 2,4,6-tri-t-butylphenyl selenide (**10**), dibutyl diselenide, and **8** (Eq. 2, Table 1).



$$\text{H}-\overset{\overset{\text{Se}}{\|}}{\text{C}}-\text{OR} + \text{ArLi} \xrightarrow{\text{THF}} \xrightarrow{\text{SiO}_2} \underset{\mathbf{9}}{\text{ArCHO}} + \underset{\mathbf{10}}{\text{ArSeBu}^n} + (n\text{-BuSe})_2 + \underset{\mathbf{8}}{\text{ArH}} \qquad (2)$$

$\text{Ar} = 2,4,6\text{-}(t\text{-Bu})_3\text{C}_6\text{H}_2$

The fact that the amounts of aldehyde **9** and dibutyl diselenide were much increased than that before the chromatography indicates the presence of an intermediate which afforded **9** and dibutyl diselenide by hydrolysis on silica gel. The intermediate is considered to be monoselenoacetal **I** formed from the reaction of initial adduct **II** with 1-bromobutane generated in the preparation of **5** (Eq. 3). The formation of **II** is reasonable by analogy with known reactivity of formates and thioformic O-esters. The appearance in ^{77}Se NMR of two signals with similar chemical shift and intensity in the reaction of **1a** also gives support to the structure of **I**, for two diastereomers due to chiral centers adjacent to the ether oxygen should exist in **1a**. Since some monoselenoacetals have been isolated,[8b,13)] the instability of monoselenoacetal **I** is probably due to its benzylic structure with high reactivity.



$$1 + 5 \longrightarrow \underset{\mathbf{II}}{\text{Ar}-\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{SeLi}}{|}}{\text{C}}}-\text{OR}} \xrightarrow{n\text{-BuBr}} \underset{\mathbf{I}}{\text{Ar}-\overset{\overset{\text{H}}{|}}{\underset{\underset{\text{SeBu}^n}{|}}{\text{C}}}-\text{OR}} \qquad (3)$$

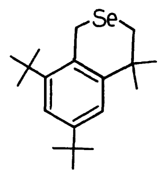
a : R = cholesteryl
b : R = t-Bu

Since the above results suggested that **II** reacted with 1-bromobutane before it was cleaved into selenoaldehyde **6** and ROLi, **5** was next prepared by the reaction of **7** with two equivalents of t-butyllithium in order to avoid the coexistence of an alkyl halide. Reactions of selenoformates **1** with **5** prepared in this way afforded results shown in Eq. 4 and Table 2.

Table 2. Reaction Products of **1a**, **1b**, and **1c** with **5** Prepared from **7** and t-Butyllithium

Run	**1**	Temp/°C	Yield/%				
			11	**9**	**12** (n=2, 3)	**13**	**8**
1	**1a**	R.t.	—	52	—	2	37
2	**1a**	60	12	5	17, 10	Trace	35
3	**1b**	R.t.	32	13	—	2	35
4	**1b**	40	44	7	—	5	28
5	**1c**	Reflux	Trace	16	Trace	8	60

$$1 + 5 \xrightarrow[\text{THF}]{-78\,^\circ\text{C}} \xrightarrow[\text{in Table 2}]{\text{Temp.}}$$



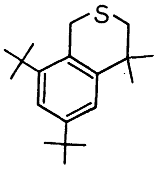
11

$$+ \underset{\mathbf{9}}{\text{ArCHO}} \qquad (4)$$

$$+ \underset{\mathbf{12}\ (n=2,\,3)}{\text{ArCH}_2\text{Se}_n\text{CH}_2\text{Ar}} + \underset{\mathbf{13}}{(\text{ArSe})_2} + \underset{\mathbf{8}}{\text{ArH}}$$

After the reaction was conducted at −78 °C, the temperature of the reaction mixture was allowed to rise as indicated in Table 2. Although the intermediate **IIa** was stable at room temperature to give aldehyde **9** by hydrolysis (Run 1), the reaction of **1a** at 60 °C gave a new product, 6,8-di-t-butyl-3,4-dihydro-4,4-dimethyl-1H-2-benzoselenin (**11**) (Run 2). In the case of **1b**, **11** was obtained even at room temperature (Runs 3 and 4). This unusual formation of dihydrobenzoselenin **11** is very interesting since it strongly suggests the intermediacy of selenoaldehyde **6**. We previously observed that thioaldehyde **4** was very stable at room temperature, but it isomerized into dihydrobenzothiopyran **14** when heated at about 200 °C.[14)] In view of this reactivity of **4**, the formation of **11** in the present reaction is most probably explicable in terms of intermediacy of **6**. The collapse of **IIb** occurred at a lower temperature than that of **IIa**, which indicated that t-BuO$^-$ anion was a more effective leaving group than cholesteryloxyl group. Since this is most likely explained in terms of steric acceleration, we next employed **1c** with the expectation that **IIc** could release Et$_3$CO$^-$ anion at a lower temperature than **IIb**. However, **IIc** was considerably stable and required reflux temper-

$$\underset{\mathbf{4}}{\text{ArCHS}} \xrightarrow{200\,^\circ\text{C}}$$



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ature for cleavage, giving only a trace amount of **11**. This is probably because steric acceleration cannot overcome the intrinsic poor reactvity of Et_3CO^- anion as a leaving group.

Since the tetrahedral intermediate **II** is more stable than a similar intermediate in the reaction of **5** with *O*-ethyl thioformate which is found to be collapsed into the thioaldehyde **4** below −30 °C, the conversion of **II** into the selenoaldehyde **6** seems to require higher temperatures where **6** can not exist as such and is isomerized to the dihydrobenzoselenin **11**. In order to collapse **II** into **6** at lower temperatures, hexamethylphosphoric triamide, dry HCl gas, or trimethylsilyl trifluoromethanesulfonate was added to the reaction mixture, but all of them were ineffective, the product in each case being aldehyde **9**.

Trapping of 6. Since selenoaldehyde **6** seemed to be too unstable to be isolated at ordinary temperature, some attempts to trap it were made. Since some thioketones[15a)] and thioaldehydes[15b)] are known to undergo the Diels-Alder reaction with dienes, 2,3-dimethylbutadiene was added to the reaction mixture with **1b** at 0 °C and the resulting mixture was allowed to warm to room temperature. However, no [4+2] adduct was obtained probably because of steric congestion by Ar group; the products were dihydrobenzoselenin **11** (18%), aldehyde **9** (17%), **12** (trace), diselenide **13** (9%), and **8** (10%).

Reactions with 1,1-dimethylhydrazine were also attempted in the hope that selenoaldehyde **6** would be reactive enough to undergo condensation with the hydrazine as it was formed. Reaction in the presence of the hydrazine, however, gave no expected hydrazone **15** but ether **16** was obtained in a reasonable yield (25%).

$ArCH{=}NNMe_2$ $ArCH_2OBu^t$ $ArCH{=}NBu^n$
15 **16** **17**

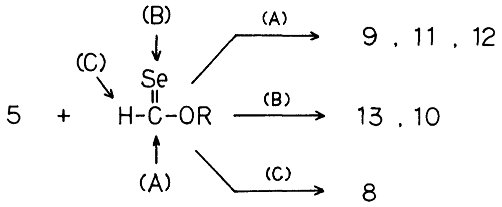
Since the ether **16** is considered to be formed by reductive cleavage of **II** by 1,1-dimethylhydrazine, the reaction with butylamine, which is a weaker reducing agent than the hydrazine, was next carried out. In this case imine **17** was obtained, though in a low yield (1.3%), along with **16** (25%).

The formation of imine **17** suggests the existence of selenoaldehyde **6** in the reaction solution, in view of similar reactivities of the corresponding thioaldehyde **4**, which reacts with butylamine at 70 °C to give **17** quantitatively.[16)] Furthermore this indicates that **6** has much greater reactivity toward amines than **4**, since **4** does not react with butylamine at room temperature.[17)]

We consider that the formation of dihydrobenzoselenin **11** and the condensation product **17** is strong evidence for the intermediacy of selenoaldehyde **6**.

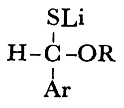
Mechanism. Since the reaction products of **5** with selenoformates **1** depend on the preparative method of **5** as described above, we classify the reactions into Case I and Case II for the convenience of the following disccussion. Case I is reactions with butyllithium as lithiating agent (Table 1) and Case II is those with *t*-buytllithium (Table 2).

Though the reactions of selenoformate **1** with **5** afford several kinds of compounds, the formation of them can be explained by three reaction paths (A)—(C) as shown in Scheme 1. These paths correspond to reactions at the selenocarbonyl carbon, the selenium, and the selenoformyl hydrogen, respectively, and the products in these paths are as follows: (A): aldehyde **9** (Cases I, II), dihydrobenzoselenin **11** (Case II), polyselenide **12** (Case II); (B): diselenide **13** (Case II), selenide **10** (Case II); (C): hydrocarbon **8** (Cases I, II). We next discuss the details of each path.



Scheme 1.

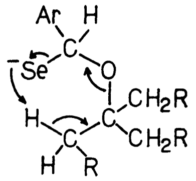
(1) Path (A). Path (A), leading to initial adduct **II**, is desirable for the formation of selenoaldehyde **6**. The fact that the reaction of **5** with *O*-ethyl thioformate gives thioaldehyde 4 at −30 °C, while that with *O*-alkyl selenoformates **1** does not afford selenoaldehyde **6** under similar conditions, indicates that the initial adduct **II** in the later reaction is thermally more stable than a similar adduct **III** in the former reaction. In Case I reaction, therefore, **II** is quenched by 1-bromobutane to give selenoacetal **I**, whose hydrolysis on silica gel leads to aldehyde **9** and *n*-BuSeH. Case II reactions afford dihydrobenzoselenin **11**, aldehyde **9**, and selenides **12** depending on the reaction temperature. The formation of **11** can be explained in terms of intermediacy of **6** as mentioned previously. The diselenide **12** (n=2) probably results from oxidative dimerization of selenol $ArCH_2SeH$ which is formed by reduction of **6** with RO^- anion (R=cholesteryl) having α-hydrogen. Similar reduction with an alkoxide ion having α-hydrogen has been reported for thioketones.[18)] The triselenide **12** (n=3) would be an oxidative coupling product between $ArCH_2SeH$ and $ArCH_2SeSeH$ which is formed by the reaction of $ArCH_2Se^-$ anion with selenium.[19)] Aldehyde **9** is thought to be formed by hydrolysis of unreacted **II** and/or by a process as shown below.



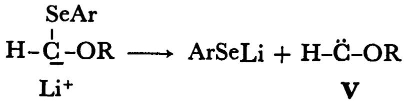
$$H-\overset{\displaystyle SLi}{\underset{\displaystyle Ar}{C}}-OR$$

III

(2) Path (B). When the addition of **5** occurs on selenium of the selenocarbonyl group, adduct **IV** is



formed (Eq. 5). The intermediate **IV** is not so stable



$$\underset{\mathbf{IV}}{\underset{\mathrm{Li^+}}{\mathrm{H{-}\overset{SeAr}{\underline{C}}{-}OR}}} \longrightarrow \mathrm{ArSeLi} + \underset{\mathbf{V}}{\mathrm{H{-}\ddot{C}{-}OR}} \qquad (5)$$

and decomposes to ArSeLi and alkoxycarbene **V**. ArSeLi thus formed is quenched by 1-bromobutane to yield **10** (Case I) or protonated to give ArSeH (Case II). ArSeH is gradually oxidized to **13** during workup. Though alkoxycarbenes have been reported to dimerize,[20] the dimer of **V** could not be found.

Such heterophilic additions of organolithium or organomagnesium reagents have been reported for thioketones and selenoketones. In the reaction of bulky 2,6-dimethylphenyllithium with di-*t*-butyl thioketone, similar decomposition of an initial adduct leading to carbenes has been observed.[21] We also reported similar formation of carbene in the reaction of 1,1,3,3-tetramethyl-2-indanselone with some Grignard reagents.[22] The bulkiness of Ar group is considered to make the decomposition even easier in the present case.

When the reaction of **1b** with **5** was carried out at −98 °C, the ratio of Se-addition/C-addition was 15/40 (Case I) or 17/26 (Case II) while the ratio of 1/10—1/20 at −78 °C. Thus the ratio of Se-addition was increased at lower temperatures. This is in keeping with the observation reported for the reaction of di-*t*-butyl thioketone with phenyllithium that the thiophilic addition is more advantageous at lower temperatures.[21]

(3) Path (C). In order to obtain direct evidence for abstraction of a selenoformyl proton of **1** by **5**, **5** was allowed to react with *O*-cholesteryl selenoformate-*d* (**1a**-***d***) having a deuterated selenoformyl group. 1,3,5-Tri-*t*-butylbenzene (**8**) thus obtained (35% yield) was analyzed for deuterium content by mass spectrometry to be 6%, providing conclusive evidence for the abstraction of the selenoformyl proton. This is, to our knowledge, the first demonstration of the proton abstraction from a selenoformyl group although formyl proton abstraction from *O*-ethyl formate[23] and that from formamides and thioformamides[24] have been reported.

Although the reason for the formation of protium species ArH is not clear at the present stage, it is probably due to proton abstraction from the solvent (THF) by unreacted **5** and/or to hydrogen abstraction by 2,4,6-tri-*t*-butylphenyl radical generated by single electron transfer from **5** to **1**.

Experimental

Melting points are uncorrected. ^{1}H (90 MHz) and ^{13}C (22.49 MHz) NMR spectra were measured in $CDCl_3$ with a JEOL FX-90Q spectrometer using tetramethylsilane as an internal standard. ^{77}Se NMR spectra were recorded at 17.03 MHz with a JEOL FX-90Q spectrometer, whose chemical shifts were measured in $CDCl_3$ with dimethyl selenide as an external standard. The mass spectra were recorded with a JEOL JMS-D300 mass spectrometer. Preparative liquid chromatography (PLC) was carried out using JAI Gel 1H columm (Japan Analytical Industry) with chloroform as solvent. All reactions were carried out under argon.

Preparation of Selenoformate 1. Selenoformates (**1a**, **b**, and **c**) were prepared by the Barton's method.[8]

O-Cholesteryl selenoformate (**1a**) was obtained in 70%; mp 128—131 °C; ^{1}H NMR δ=12.07 (HC=Se) (δ=12.15 in Ref. 8); ^{77}Se NMR δ=1006. *O*-*t*-Butyl selenoformate (**1b**) (22%) was recrystallized from hexane at −30 °C; mp 50.5—51.5 °C; ^{1}H NMR δ=1.57 (9H, s, *t*-Bu) and 12.20 (1H, s, HC=Se); ^{13}C NMR δ=28.4 [$C(\underline{C}H_3)_3$], 89.5 [$\underline{C}(CH_3)_3$], and 215.0 (C=Se); ^{77}Se NMR δ=1052; MS *m/z* (rel intensity) 166 (M^+, 12) and 57 (100). Found *m/z* 165.9903. Calcd for $C_5H_{10}O^{80}Se$: M, 165.9897. *O*-(1,1-Diethylpropyl) selenoformate (**1c**) (6.5%) was obtained as an orange oil after Kugelrohr distillation (70 °C, 0.05 mmHg).[#] ^{1}H NMR δ=0.92 (9H, t, *J*=7 Hz), 1.84 (6H, q, *J*=7 Hz), and 12.14 (1H, s, $\underline{H}$C=Se); MS *m/z* (rel intensity) 208 (M^+, 2), 99 (50), 69 (76), 57 (100), and 55 (59). Found *m/z* 208.0371. Calcd for $C_8H_{16}O^{80}Se$: M, 208.0366.

Preparation of ArLi (5). I) *n*-BuLi (1 equiv) was added to a solution of ArBr (**7**)[25] (1 equiv) in THF at −78 °C and the resulting mixture was stirred for 15 min at −78 °C before use. **5** prepared in this way is denoted as ArLi(I). II) *t*-BuLi (2 equiv) was added to the solution of **7** (1 equiv) in THF at −78 °C and the resulting yellow solution was stirred at −78 °C till the yellow color disappeared (ca. 1 h). **5** prepared by this method is denoted as ArLi(II).

Reactions of 1 with ArLi(I). (a) A solution of **1a** (0.331 g, 0.693 mmol) in THF (3 ml) was added to ArLi(I) (0.631 mmol) in THF (5 ml) at −78 °C during 5 min. The mixture was stirred at this temperature for 30 min. The yellow reaction mixture was warmed to room temperature to give an orange red solution. After stirring for 30 min at this temperature, water and ether were added. The ethereal extract was washed with water and dried ($MgSO_4$). Removal of the solvent under reduced pressure left 0.497 g of an orange solid, whose ^{77}Se NMR showed major peaks at δ 360 and 364, and other small peaks at δ 224 (ArSeBu^n, **10**), 313 $(n\text{-BuSe})_2$, and 345, 349, 491, and 498 (unknown). This crude reaction mixture was subjected to chromatography (silica gel, hexane–dichloromethane 10:1). The first yellow fraction was separated again by PLC to afford ArH (**8**) (44.9 mg, 29%), dibutyl diselenide[26] (53.2 mg, 62%), and ArSeBu^n **10** (10.9 mg, 4.5%). **10** was recrystallized from ethanol giving colorless crystals. They once melted at 67.5—68.0 °C and crystallized again. These second crystals melted at 77.5—78.0 °C. ^{1}H NMR δ=0.80—1.61 [34H, m; 18H for *o*-*t*-Bu (δ=1.61), 9H for *p*-*t*-Bu (δ=1.30), 3H for $ArSe(CH_2)_3\text{-}\underline{CH_3}$ (δ=0.87, t, *J*=7 Hz), and 4H for $ArSeCH_2C\underline{H_2}C\underline{H_2}CH_3$ (m)], 2.46 (2H, t, *J*=8 Hz, $ArSeC\underline{H_2}CH_2CH_2CH_3$), 7.37 (2H, s, aromatic); MS *m/z* (rel intensity) 382 (M^+, 25), 367 (4), 336

[#] 1 mmHg=133.322 Pa.

(2), 311 (4), and 57 (100). Found: C, 69.08; H, 10.29%. Calcd for $C_{22}H_{38}Se$: C, 69.26; H, 10.04%. The second fraction was purified by PLC to give ArCHO (**9**)[27] (83.4 mg, 48%): Mp 189.5—190.5 °C after recystallization from methanol. ^{1}H NMR δ=1.32 (9H, s, *p*-*t*-Bu), 1.36 (18H, s, *o*-*t*-Bu), 7.37 (2H, s, aromatic), and 11.11 (1H, s, $C\underline{H}O$); ^{13}C NMR δ=202.7 ($\underline{C}HO$), 150.8, 147.4, 137.2, 36.6, 35.1, 32.6, and 31.3; MS *m*/*z* (rel intensity) 274 (M$^+$, 22), 259 (100), 241 (45), 217 (42), and 57 (72). Found: C, 82.94; H, 10.97%. Calcd for $C_{19}H_{30}O$: C, 83.15; H, 11.02%.

(b) A solution of **1b** (0.133 g, 0.803 mmol) in THF (1 ml) was added to ArLi(I) (0.804 mmol) in THF (5 ml) at −98 °C. The reaction mixture was stirred for 20 min at −98 °C and warmed to room temperature and to this was added aqueous ammonium chloride and ether. The ethereal extract was washed with water and dried ($MgSO_4$). Removal of the solvent gave 0.358 g of an orange oil, whose ^{77}Se NMR showed a peak at δ 442. This reaction mixture was subjected to chromatography (silica gel, hexane–dichloromethane, 10:1). The first fraction contained **8**, **10**, and dibutyl diselenide, whose yields were determined by ^{1}H NMR to be 18, 15, and 55%, respectively. The second fraction was **9** (87.1 mg, 40%).

Reactions of 1 with ArLi(II). (a) A THF solution of **1a** (0.474 g, 0.992 mmol) in THF (5 ml) was added to ArLi(II) (0.902 mmol) in THF (10 ml) at −78 °C during 10 min. The resulting reaction mixture was stirred for 20 min at this temperature and warmed to room temperature. To the red solution was added aqueous ammonium chloride and ether, when much red selenium was precipitated. The organic layer was washed with water and dried ($MgSO_4$). After removal of the solvent, the residue was subjected to chromatography (silica gel, hexane–dichloromethane 10:1) and PLC to give **9** (129 mg, 52%), **8** (81.2 mg, 37%), and $(ArSe)_2$ (**13**)[28] (5.2 mg, 2%). **13** was recrystallized from ethanol giving an orange crystal: Mp 251.2—253.2 °C. ^{1}H NMR δ=1.28 (36H, s, *o*-*t*-Bu), 1.32 (18H, bs, *p*-*t*-Bu), and 7.25 (4H, s, aromatic); ^{77}Se NMR δ=521; MS *m*/*z* (rel intensity) 650 (M$^+$, 7), 326 (8), and 57 (100). Found: *m*/*z* 650.2887. Calcd for $C_{36}H_{58}{}^{80}Se_2$: M, 650.2867.

The following reactions were carried out in a similar way.

(b) **1a** (0.447 g, 1.00 mmol) was reacted with ArLi(II) (1.00 mmol). The resulting reaction mixture was heated to 60 °C and stirred at this temperature for 12 h. Products were dihydrobenzoselenin **11** (40 mg, 12%), $ArCH_2Se_nCH_2Ar$ (**12**, 130 mg, from ^{1}H NMR *n*=2, 17%; *n*=3, 10%), **9** (14.8 mg, 5%), **13** (trace), and **8** (85.5 mg, 35%). **11** was recrystallized from ethanol to give colorless needles: Mp 180.5—181.0 °C; ^{1}H NMR δ=1.32 (9H, s, *t*-Bu), 1.47 (9H, s, *t*-Bu), 1.53 [6H, s, $SeCH_2C(C\underline{H}_3)_2$], 2.76 [2H, s, $SeC\underline{H}_2C(CH_3)_2$], 4.04 (2H, s, benzyl), and 7.35 (2H, s, aromatic); ^{13}C NMR δ=147.8, 145.9, 145.9, 131.8, 121.2, 121.3, 38.0, 35.9, 34.9, 32.8, 31.9, 31.5, 30.6, and 18.2; ^{77}Se NMR δ=89.3; MS *m*/*z* (rel intensity) 338 (M$^+$, 34), 323 (13), 281 (18), 229 (14), and 57 (100). Found: C, 67.36; H, 9.07%. Calcd for $C_{19}H_{30}Se$: C, 67.64; H, 8.96%. Found: *m*/*z* 338.1500. Calcd for $C_{19}H_{30}{}^{80}Se$: M, 338.1511. **12**, a mixture of selenides, was dissolved in methanol. Insoluble orange solid contained triselenide (**12**, *n*=3) as judged by mass spectroscopy and showed peaks at δ 512, 521, 619, and 719 in ^{77}Se NMR. From the filtrate was obtained diselenide (**12**, *n*=2) after repetitive recrystallization from ethanol–hexane: Yellow crystals, mp 150.0—152.0 °C. ^{1}H NMR δ=1.58 (36H, s, *o*-*t*-Bu), 1.30 (18H, s, *p*-*t*-Bu), 5.05 (4H, s, benzyl), and 7.33 (4H, s, aromatic); ^{77}Se NMR δ=412; MS *m*/*z* (rel intensity) 678 (M$^+$, 0.1), 259 (38), 243 (100), 149 (19), and 57 (93). Found: C, 67.51; H, 9.53%. Calcd for $C_{38}H_{62}Se_2$: C, 67.43; H, 9.23%.

(c) **1b** (0.113 g, 0.684 mmol) in THF (2 ml) was added to ArLi(II) (0.683 mmol) in THF (5 ml) at −78 °C. The resulting reaction mixture was warmed to room temperature and stirred at this temperature for 1 h. Products were **11** (74.5 mg, 32%), **9** (32.5 mg, 13%), **13** (5.4 mg, 2%), and **8** (58.6 mg, 35%).

(d) **1b** (0.111 g, 0.670 mmol) in THF (2 ml) was added to ArLi(II) (0.699 mmol) in THF (5 ml) at −78 °C. The resulting red reaction mixture was heated to 40 °C and stirred at this temperature for 30 min. Products were **11** (100 mg, 44%), **9** (13.6 mg, 7%), **13** (11.3 mg, 5%), and **8** (61.0 mg, 28%).

(e) **1b** (0.083 g, 0.50 mmol) in THF (1 ml) was added to ArLi(II) (0.50 mmol) at −98 °C. The reaction mixture was heated to 60 °C and to this was added water. **11** was obtained in 26% (43 mg). **8** was obtained as a mixture with **13** and ArSeH. This mixture was stirred with KOH (1 grain) in dichloromethane and methanol in order to convert ArSeH to **13**. Separation by PLC yielded **8** (30 mg, 25%) and **13** (27 mg, 17%).

(f) **1c** (0.104 g, 0.500 mmol) in THF (0.5 ml) was added to ArLi(II) (0.503 mmol) in THF (5 ml) at −78 °C. The resulting orange reaction mixture was stirred at room temperature for 12 h and at reflux for 16 h. Products were **11** (trace), **9** (22 mg, 16%), **12** (trace), **13** (13 mg, 7.8%), and **8** (74 mg, 60%).

Reaction of 1 and 5 with Hexamethylphosphoric Triamide (HMPA). (a) A solution of **1a** (0.400 g, 0.838 mmol) in THF (5 ml) was added to ArLi(II) (0.757 mmol) in THF (5 ml) at −78 °C. The yellow reaction mixture was stirred at this temperature for 1 h and was added HMPA (1.44 g, 8.00 mmol) at −78 °C. The orange reaction mixture was warmed to room temperature and stirred at room temperature for 2 d. TLC of the reaction mixture showed that **11** was not formed. Silica-gel chromatography and PLC gave **9** (76.2 mg, 37%), **12** (trace), **13** (trace), and **8** (89.7 mg, 48%).

(b) A solution of **1b** (0.172 g, 0.680 mmol) in THF (2 ml) was added to ArLi(II) (0.680 mmol) at −78 °C. The reaction mixture was warmed to 0 °C and again cooled to −78 °C. To the red orange reaction mixture was added HMPA (0.72 g, 4.0 mmol). The temperature of the resulting mixture was allowed to rise to −30 °C and stirred at this temperature for 1 h, and to this was added water. Silica-gel chromatography and PLC afforded **9** (59.9 mg, 36%), **13** (11.4 mg, 5%), and **8** (81.8 mg, 49%).

Reaction of la and 5 with Dry HCl Gas. A solution of **1a** (0.321 g, 0.673 mmol) in THF (5 ml) was added to ArLi(II) (0.619 mmol) in THF (5 ml) at −78 °C. The reaction mixture was allowed to rise to room temperature. The solvent was removed in vacuo and dichloromethane (15 ml) was added. The resulting reaction mixture was cooled to −78 °C and excess dry HCl gas was bubbled into it. The yellow suspension was warmed to room temperature. When dichloromethane was removed in vacuo, a gas of unpleasant smell was detected (probably hydrogen selenide, absorbed by KOH). Products were **9** (70.0 mg, 41%), **13** (trace), and **8** (83.0 mg, 54%).

Reaction of 1b and 5 with Trimethylsilyl Trifluoromethanesulfonate (TMSOTf). A solution of **1b** (0.106 g, 0.643 mmol) in THF (2 ml) was added to ArLi(II) (0.643 mmol) in THF (5 ml) at −78 °C. The reaction mixture was warmed to 0 °C. The solvent was removed in vacuo and dichloromethane (10 ml) was added. The yellow suspension was warmed to room temperature and stirred for 18 h. TLC showed no **11**. Additional TMSOTf (0.146 g, 0.657 mmol) was added at 0 °C and the mixture was stirred for 10 h at room temperature. **9** (62.1 mg, 35%), **13** (7.8 mg, 4%), and **8** (84.2 mg, 53%) were obtained.

Trapping Reaction of 6 with Butylamine. A solution of **1b** (95.8 mg, 0.58 mmol) in THF (1 ml) was added to ArLi(II) (0.579 mmol) in THF (5 ml) at −78 °C. The reaction mixture was warmed to 0 °C and to this was added butylamine (0.422 g, 5.77 mmol) in THF (1 ml). The resulting reaction mixture was stirred for 2 h at room temperature. After the addition of water and ether, the separated ethereal layer was washed successively with dil HCl, dil aqueous sodium carbonate, and water, and dried ($MgSO_4$). After chromatographic separation, there were obtained imine **17** (2.5 mg, 1.3%), ether **16** (47.8 mg, 25%), **9** (16.2 mg, 10%), **12** (trace), **13** (12.9 mg, 7%), and **8** (62.3 mg, 48%). **17** was identified by comparing its ^{1}H NMR spectrum with that of an authentic sample.[16] **16** was recrystallized from ethanol–water to give colorless crystals: Mp 94.8—95.4 °C; ^{1}H NMR δ=1.29 (9H, s),1.34 (9H, s), 1.52 (18H, s), 4.86 (2H, s, benzyl), and 7.41 (2H, s, aromatic); MS *m/z* (rel intensity) 332 (M^+, 7.6), 259 (7.6), 247 (18), 219 (56), and 57 (100). Found: *m/z* 332.3076. Calcd for $C_{23}H_{40}O$: M, 332.3077.

An Attempt to Trap 6 with 2,3-Dimethyl-1,3-Butadiene. A solution of **1b** (0.100 g, 0.608 mmol) in THF (1 ml) was added to ArLi(II) (0.607 mmol) in THF (5 ml) at −78 °C. The reaction mixture was stirred at this temperature for 30 min and warmed to 0 °C. 2,3-Dimethyl-1,3-butadiene (0.508 g, 6.3 mmol) in THF (1 ml) was added and the resulting mixture was stirred for 2 h at room temperature. Chromatographic purification gave **11** (37.8 mg, 18%), **9** (28.4 mg, 17%), **12** (trace), **13** (8.6 mg, 9%), and **8** (69.8 mg, 47%).

An Attempt to Condense 6 with 1,1-Dimethylhydrazine. A solution of **1b** (94.4 mg, 0.602 mmol) in THF (1 ml) was added to ArLi(II) (0.602 mmol) in THF (5 ml) at −78 °C. The reaction mixture was stirred for 30 min at this temperature and warmed to 0 °C. 1,1-Dimethylhydrazine (0.364 g, 6.05 mmol) in THF (1 ml) was added and the resulting reaction mixture was stirred for 1.5 h at room temperature. Products obtained were **16** (50.7 mg, 25%), **9** (19.9 mg, 12%), **13** (16.1 mg, 18%), and **8** (80.0 mg, 54%).

O*-Cholesteryl Selenoformate-*d* (1a-*d*).** **1a-*d was prepared in 67% yield by the Barton's method, using *N,N*-dimethylformamide-d_7 (99%, Merck) instead of *N,N*-dimethylformamide in preparation of imidoyl chloride: Mp 135—137 °C (after recrystallization from hexane); ^{1}H NMR δ= 0.69—2.28 (43H, m), 2.50—2.60 (2H, bd), and 5.30—5.78 (2H, m). Selenoformyl proton was observed at δ=12.06 but negligibly small. ^{77}Se NMR δ=1000.

Reaction of *O*-Cholesteryl Selenoformate-*d* (1a-*d*) with 5. A solution of **1a-*d*** (0.319 g, 0.666 mmol) in THF (3 ml) was added to ArLi(II) (0.619 mmol) in THF (10 ml) at −78 °C. The reaction mixture was heated to 60 °C and stirred at this temperature for 20 h. Chromatographic purification afforded a mixture of ArH (**8**) and ArD (**8-*d***) (53.7 mg, 35%). The ratio of **8**/**8-*d*** was 94/6 (by mass spectrum).

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