Unexpected Leaving Ability of (Phenyltelluro)formates in the Presence of Internal Nucleophiles: Complications during Alkyl and Oxyacyl Radical Generation in the Preparation of Sulfur- and Selenium-Containing Heterocycles

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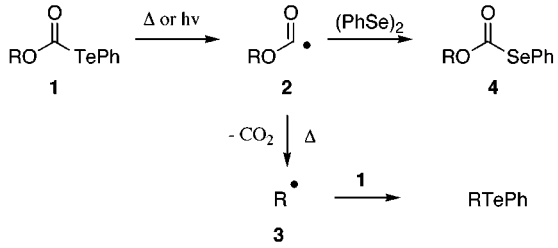
Irradiation of a benzene solution of 1-(benzylseleno)-3-undecyl (phenyltelluro)formate (**13**) with a 250-W low-pressure mercury lamp leads to the formation of 4-octyl-3-oxaselenan-2-one (**18**) in good yield. This transformation represents the first reported example of intramolecular homolytic substitution by oxyacyl radicals at selenium. The analogous reaction involving 1-(benzylseleno)-4-dodecyl (phenyltelluro)formate (**14**) provides a complex mixture of products, while thermolysis of a benzene solution of **14**, 1-(benzylseleno)-5-tridecyl (phenyltelluro)formate (**15**) or 1-(benzylseleno)-6-tetradecyl (phenyltelluro)formate (**16**) at 160° affords 2-octyltetrahydroselenophene (**21**), 2-octylselenane (**22**), and 2-octylselenopane (**23**) in 43−94% yield, respectively. The formation of the saturated selenium-containing heterocycles **21**−**23** is most likely to involve nucleophilic attack by the benzylseleno moiety with (decarboxylative) expulsion of phenyltelluride. The mechanisms of these transformations are discussed.

Introduction

Methods of generating carbon-centered radicals from alcohols are synthetically significant because they allow not only for deoxygenations, but also for the formation of carbon−carbon bonds via inter- and intramolecular homolytic addition chemistry.[1−12] Free-radical precursors derived from alcohols include dithio- and thionocarbonates (primary and secondary alcohols)[5,6] and thiohydroxamic (Barton) esters derived from oxalates (tertiary alcohols).[7] Chain carriers such as tributyltin hydride are often used in this chemistry and, as is the case with most radical chemistry, a disparity of reactivities between the chain carrier (Bu_3SnH), the intended radical precursor, and other functionality in the substrate is required for success.[1,13]

Scheme 1



During recent work aimed at the preparation of selenium-containing heterocycles,[13−18] we required a method for the generation of alkyl radicals from alcohols in the presence of the benzylseleno moiety. We reported recently that aryltelluroformates **1** are photochemically and thermally labile and are effective radical precursors of oxyacyl radicals **2** which, depending on reaction conditions, can decarboxylate to afford alkyl radicals **3** (Scheme 1).[17]

Prior to this work, the most common method for the formation of oxyacyl radicals involved the use of seleno-formates **4** under stannane-mediated conditons.[19−21] Unlike telluroformates **1** the seleno analogues are photo-

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(2) Barton, D. H. R. *Half a Century of Free Radical Chemistry*; Cambridge University Press: Cambridge, UK, 1993.

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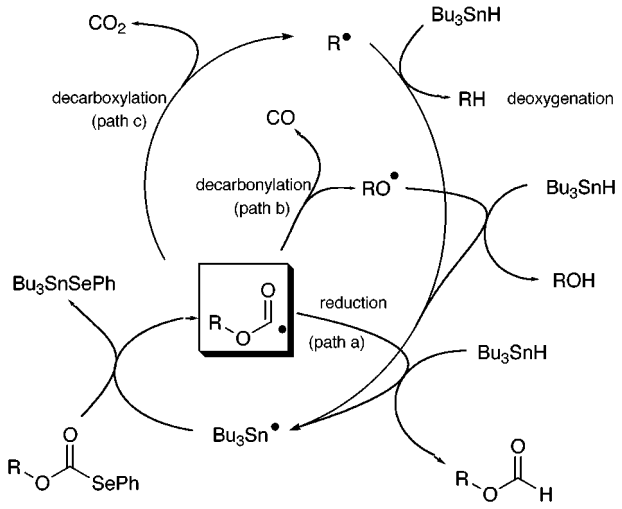
Scheme 2



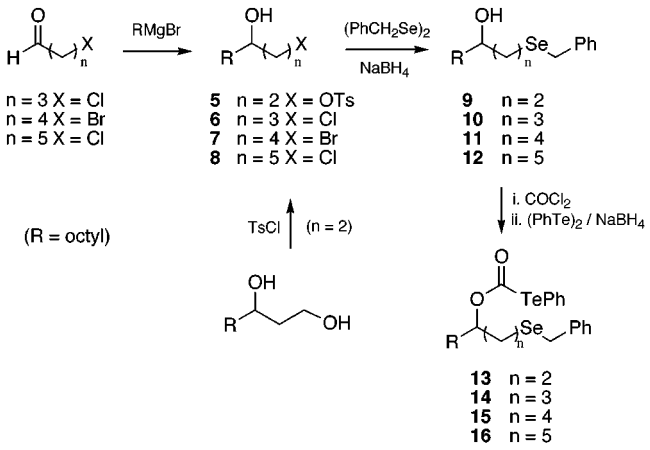
chemically and thermally stable and require the use of chain-carrying radicals such as tributylstannyl to induce oxyacyl radical formation.[19−21] Under these conditions the oxyacyl radicals are subject to several competing pathways (Scheme 2). These include reduction (path a), decarbonylation (path b), and decarboxylation (path c). This competition has consequently limited their use in synthetic strategies. Pfenninger and co-workers acknowledged this dilemma but illustrated that the ratio of products can be controlled to some extent by manipulating reaction temperature.[19] It was their belief that the greater preparative significance of selenoformates lay in their use as free-radical precursors strictly for the formation of deoxygenated products. Some years later Bachi and Bosch[20,21] demonstrated that selenoformates can serve as a synthetically useful source of oxyacyl radicals by inducing intramolecular addition chemistry to form various δ- and γ-lactones. The development of the telluoformate precursor has facilitated access to oxyacyl radicals without the need for chain-carrying radicals. In addition to this, under photolytic conditions at room-temperature, decarbonylation and decarboxylation are not significant processes; this was illustrated by the quantitative formation of selenoformates **4** from the corresponding alkyltelluroformates **1** upon addition of diphenyldiselenide (Scheme 1).

In this paper, we expand upon our initial thermolytic and photolytic investigations of telluroformates and demonstrate that under appropriate conditions they are useful sources of oxyacyl radicals but prefer to act as leaving groups at elevated temperatures and in the presence of internal nucleophiles.

Results and Discussion

Preparation of (Phenyltelluro)formates. Given our previous experience with saturated selenium-containing heterocycles,[18] in particular their volatility and azeotropic properties, we chose to examine systems of significantly greater molecular weight in this study. Octyl-substituted substrates **13**−**16** which would afford heterocycles **18**, **21**−**23** appeared to meet our requirements. (Phenyltelluro)formates **13**−**16** were prepared according to the general procedure outlined in Scheme 3. To that end, 4-chlorobutanal, 5-bromopentanal, and 6-chlorohexanal were reacted with octylmagnesium bromide under standard Grignard conditions to afford the halo alcohols **6**−**8** in high yield. Undecane-1,3-diol[22] was converted to the primary tosylate **5** under standard conditions.

Scheme 3



Conversion of alcohols **5**−**8** to the corresponding benzylseleno alcohols **9**−**12** was accomplished using sodium benzylselenoate.[13,18] These selenides are readily identified through the use of ^{77}Se NMR spectroscopy as they exhibit a characteristic single signal in the range 253−259 ppm ($CDCl_3$).

Telluroformates **13**−**16** were prepared by the treatment of alcohols **9**−**12** with a solution of phosgene in toluene followed by sodium phenyltelluroate[17] and were isolated as yellow/orange viscous oils in yields of 50−74%. They are readily characterized by ^{125}Te and ^{77}Se NMR spectroscopy and typically display signals at δ 756−765 (^{125}Te) and 257−267 (^{77}Se) (C_6D_6) and are stable for indefinite periods refrigerated and shielded from background light.

Harnessing Oxyacyl Radicals: Preparation of 4-Octyl-3-oxaselenan-2-one (18). As discussed previously, photolysis of telluroformates **1** leads to the formation of oxyacyl radicals **2** which can be trapped by diphenyl diselenide to give the corresponding selenoformate **4**. Importantly, at room-temperature decarboxylation (and decarbonlyation) of **2** was found not to be competitive with homolytic attack at selenium to afford **4**.[17] With this in mind, we reasoned that the oxyacyl radical **17** could be trapped internally to afford the hitherto unknown oxaselenanone ring-system (**18**).

When 1-(benzylseleno)-2-undecyl (phenyltelluro)formate (**13**) was dissolved in benzene-d_6 (0.15 M) and irradiated at room temperature with a 250 W low-pressure mercury lamp (white light) as previously described[17] and the reaction monitored by ^{1}H NMR spectroscopy, complete consumption of starting material **13** was observed after 64 h. This time frame is consistent with photolyses of other telluroformates carried out at this concentration.[17] Analysis of the reaction mixture by TLC revealed a single major component which was isolated in 73% yield by preparative TLC and proved to be 4-octyl-3-oxaselenan-2-one (**18**) (Scheme 4). Presumably the oxyacyl radical **17** undergoes intramolecular homolytic substitution at selenium to afford **18**; this transformation represents the first example of such a

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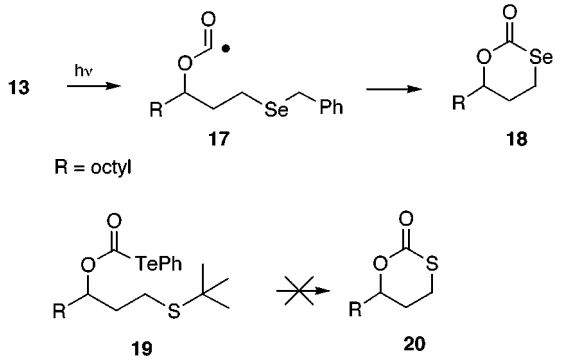
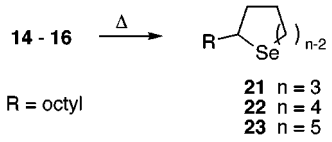
Scheme 4



Scheme 5



reaction involving oxyacyl radicals. It is interesting to note that the ^{77}Se NMR spectrum of **18** reveals a single resonance at δ 307.5, presumably characteristic of the (previously) unknown 3-oxaselenan-2-one ring system.

Unfortunately, similar experiments using 1-(benzylseleno)-3-dodecyl (phenyltelluro)formate (**14**) resulted in none of the anticipated 4-octyl-3-oxaselenopan-2-one, rather a complex mixture of products was observed by TLC and NMR analysis, as well as large quantities of a black precipitate, presumably elemental tellurium. Similar results were obtained in the attempted preparation of 4-octyl-3-oxathian-2-one (**20**) from telluroformate **19** under similar reaction conditions. The rate of ring-closure may well be crucial to the success of these reactions. Formation of the six-membered selenium-containing ring (**18**) would appear to be favored over the analogous seven-membered ring, an observation we have reported previously in other systems,[18] while intramolecular homolytic substitution at sulfur is well established to be some 3 orders of magnitude slower than the analogous reaction at selenium;[23] formation of the sulfur-containing ring might be expected to be disfavored.

It is interesting to note that thermolysis of **13** at 160° in the dark resulted in an approximately 56% conversion to **18** after 79 h as determined by ^{1}H NMR spectroscopy while photolysis of **14** at 80° resulted in the smooth formation of 2-octyltetrahydroselenophene (**21**) (Scheme 5), presumably via the corresponding alkyl radical, despite our previous observations that oxyacyl radicals decarboxylate only very slowly at 80°. This observation is discussed in further detail below.

Thermally Induced Ring Closure. Preparation of Saturated Selenium-Containing Ring Systems. In our previous study, temperatures of around 160° and concentrations greater than about 0.5 M were found to be necessary for synthetically viable transformations involving decarboxylation of oxyacyl radicals.[17] Indeed, 2-methylselenane (**22**, R = Me) was prepared by heating a 0.7 M solution of 1-(benzylseleno)-5-hexyl (phenyltelluro)formate in benzene at 160° in a sealed tube for 14 days and isolated as the 1,1-dibromide (due to volatility problems) in 74% yield. In similar fashion, 1-(benzylseleno)-4-dodecyl (phenyltelluro)formate (**14**) was dissolved in benzene (0.46 M) and the solution heated at 160° in a sealed-tube for 2 days. To our delight, ^{1}H NMR spectroscopy of the crude reaction mixture indicated quantitative conversion to 2-octyltetrahydroselenophene (**21**) which was isolated in 87% yield after chromatography. Similarly, 1-(benzylseleno)-5-tridecyl (phenyltelluro)formate (**15**) (1.05 M) afforded 2-octylselenane (**22**) in 94% yield after 12 days at 160°.

When 1-(benzylseleno)-6-tetradecyl (phenyltelluro)formate (**16**) (0.79 M) was subjected to the same conditions, a much slower reaction was observed. ^{1}H NMR spectroscopy not only revealed that 20 days was required for complete consumption of the starting telluroformate **16** but that a complex mixture of products had formed; 2-octylselenopane (**23**) was isolated in 43% yield after chromatography.

Close ^{1}H NMR monitoring of the (160°) thermolysis reactions of **14** (0.46 M) and **15** (1.05 M) provide reactions half-lives of 2 and 44 h, respectively. In previous work, we had established that secondary telluroformates (**1**, R = secondary alkyl) react at 160° to afford the corresponding alkyl phenyltelluride with similar half-lives at a given concentration,[17] a result consistent with decarboxylation of **2** to afford **3** being the rate-determining step in the mechanistic sequence.[17] From this work, it is possible to estimate the reaction half-lives for the telluroformates in this study;[24] values of 3.5 days, 20 h, and 1.5 days are estimated for reactions performed at 0.46, 1.05, and 0.79 M concentration, respectively.

On first inspection, it seems reasonable to attribute the formation of the selenium-containing heterocycles **21**−**23** to intramolecular homolytic substitution by alkyl radicals at selenium. Closer inspection of the available information, however, may require an alternative explanation. Why do the thermolyses of **14**−**16** proceed at rates significantly different from each other and from the reactions performed in our previous study? The answer to this question must lie with changes in the reaction mechanism, specifically that the rate determining step in the reactions involving **14**−**16** must be different from that in our previous study.

Alkyl selenides are significantly nucleophilic. We recently demonstrated that benzoselenazine-2,4-diones can be formed through intramolecular addition/elimination of a benzylseleno moiety at the electrophilic center in a carbamoyl chloride.[25] It seems reasonable to suggest, therefore, that the saturated selenium-containing rings (**21**−**23**) are being formed through intramolecular *nucleophilic* substitution of the benzylseleno moiety in telluroformates **14**−**16** with decarboxylative loss of phenyl telluride (Scheme 6), the overall result being identical to that depicted in Scheme 5. Formation of the five-, six- and seven-membered rings will have different energy requirements leading to different overall reaction rates. The formation of **21** at 80° is also rationalized; the unfavorable decarboxylation of the oxyacyl radical **17** is no longer required. It would seem, therefore, that formation of 2-methylselenane reported previously by us[17] is also most likely to be the result of nucleophilic chemistry.

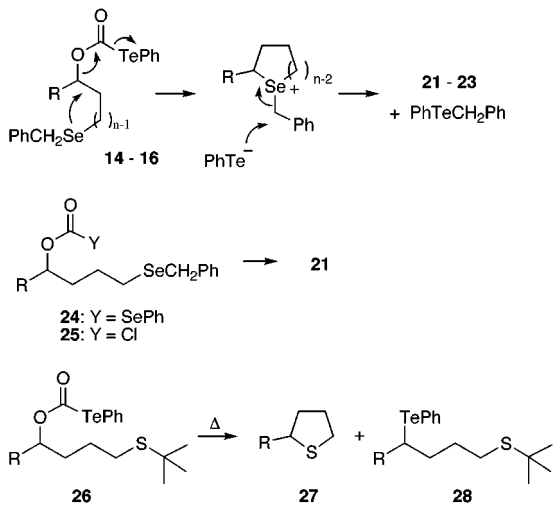
To assess the validity of this mechanism, the corresponding selenoformate **24** and chloroformate **25**, func-

(23) Schiesser, C. H.; Wild, L. M. *Tetrahedron* **1996**, *52*, 13265.

(24) Figure 2, reference 17.

(25) Fong, M. C.; Laws, M. J.; Schiesser, C. H. *Aust. J. Chem.* **1995**, *48*, 1221.

Scheme 6



tionalities known not to produce oxyacyl radicals upon thermolysis at 160°,[17] were thermolyzed in benzene-d_6 (sealed NMR tube) and the reaction outcome monitored by ^{1}H NMR spectroscopy. Quantitative formation of 2-octyltetrahydroselenophene together with benzyl phenylselenide or benzyl chloride was observed after about 5 days, providing clear evidence of a nucleophilic mechanism involved in the formation of the tetrahydroselenophene.

While telluroformates clearly can function as sources of both alkyl and oxyacyl radicals,[17] this work has demonstrated that under appropriate conditions, they can also function as leaving groups in nucleophilic chemistry. In the presence of a less nucleophilic functional group, the formation of alkyl radicals should be much more competitive. To explore this possibility, 1-(*tert*-butylthio)-4-dodecyl (phenyltelluro)formate (**26**), containing the much less nucleophilic *tert*-butylthio substituent, was heated in benzene-d_6 (0.46 M) in a sealed NMR tube. ^{1}H NMR spectroscopy revealed the absence of the starting material after 32 h and the formation of a complex mixture which included 2-octyltetrahydrothiophene (**27**). Flash chromatography afforded **27** in 43% yield (contaminated with small amounts of diphenyl ditelluride and other contaminants) as well as 1-(*tert*-butylthio)-4-(phenyltelluro)dodecane (**28**, 14%). While the formation of **27** and **28** is consistent with the involvement of alkyl radicals which either undergo intramolecular homolytic substitution at sulfur or intermolecular homolytic substitution (chain propagation) at another molecule of starting telluroformate **26**, the reaction time of 32 h is somewhat shorter than the expected half-life of 3.5 days,[17] suggesting that ring-closure is once-again proceeding, to a large extent, via nucleophilic substitution.

Experimental Section

Diphenyl ditelluride[26] was prepared according to published procedures. All melting points and boiling points are uncorrected. NMR spectra were recorded in benzene-d_6 unless otherwise stated. Elemental analyses were carried out by Chemical and Micro Analytical Services Pty. Ltd.

1-(Benzylseleno)-3-undecyl (phenyltelluro)formate (13) was prepared according to standard protocol (B) in our previously published paper[17] using 1-(benzylseleno)-3-undecanol (**9**). Flash chromatography (hexane/ethyl acetate 95:5) aforded **13** as a yellow oil (52%): ^{1}H NMR δ 0.92 (3H, t, J = 6.6 Hz), 1.12−1.38 (15H, m), 1.55 (1H, m), 1.72 (1H, m), 2.29 (2H, m), 3.47 (1H, s), 5.15 (1H, m), 6.94−7.16 (8H, m), 7.80 (2H, m); ^{13}C NMR δ 14.34, 19.25, 23.04, 25.62, 27.16, 29.60, 29.65, 29.74, 32.21, 34.32, 35.55, 78.95, 114.16, 126.84, 128.69, 128.90, 129.22, 129.54, 139.85, 139.97, 156.42; ^{77}Se NMR δ 266.9; ^{125}Te NMR δ 764.2; IR ν (neat) 1709 cm^{-1}; MS m/z (relative intensity) 574 (M^+, 0.04), 325 (6), 206 (4), 91 (100). Anal. Calcd for $C_{25}H_{34}O_2SeTe$: C, 52.40; H, 5.98. Found: C, 52.47, H, 5.96.

1-(Benzylseleno)-4-dodecyl (phenyltelluro)formate (14) was prepared according to standard protocol (B) in our previously published paper[17] using 1-(benzylseleno)-4-dodecanol (**10**). Flash chromatography (hexane/ethyl acetate 98:2) afforded **14** as a yellow oil (61%): ^{1}H NMR δ 0.92 (3H, t, J = 6.9 Hz), 1.71−1.58 (18H, m), 2.22 (2H, t, J = 6.9 Hz), 3.51 (2H, s), 5.10 (1H, m), 6.93−7.18 (8H, m), 7.80 (2H, d, J = 7.5 Hz); ^{13}C NMR δ 14.38, 23.07, 23.53, 25.76, 26.30, 26.98, 29.65, 29.73, 29.81, 32.23, 34.67, 78.72, 114.20, 126.79, 128.64, 128.88, 129.22, 129.54, 139.97, 156.47; ^{77}Se NMR δ 257.3; ^{125}Te NMR δ 762.3; IR ν (neat) 1708 cm^{-1}; MS (20 eV) m/z (relative intensity) 587 (M^+, 1.2), 452 (6), 339 (77), 91 (100). Anal. Calcd for $C_{26}H_{36}O_2SeTe$: C, 53.19; H, 6.18. Found: C, 53.21, H, 6.08.

1-(Benzylseleno)-5-tridecyl (phenyltelluro)formate (15) was prepared according to standard protocol (B) in our previously published paper[17] using 1-(benzylseleno)-5-tridecanol (**11**). Flash chromatography (hexane/ethyl acetate 98:2) aforded **15** as a yellow oil (71%): ^{1}H NMR δ 0.92 (3H, t, J = 7.2 Hz), 1.20−1.45 (20H, m), 2.21 (2H, t, J = 7.2 Hz), 3.52 (2H, s), 5.12 (1H, m), 6.93−7.19 (8H, m), 7.82 (2H, d, J = 7.5 Hz); ^{13}C NMR δ 14.37, 23.05, 23.55, 25.78, 25.93, 26.97, 29.64, 29.75, 29.82, 30.20, 32.22, 34.10, 34.67, 79.03, 114.21, 126.76, 128.62, 128.86, 129.23, 129.52, 139.99, 140.07, 156.47; ^{77}Se NMR δ 260.0; ^{125}Te NMR δ 761.1; IR ν (neat) 1709 cm^{-1}; MS m/z (relative intensity) 467 (1), 352 (2), 91 (100). Anal. Calcd for $C_{27}H_{38}O_2SeTe$: C, 53.95; H, 6.37. Found: C, 53.97, H, 6.32.

1-(Benzylseleno)-6-tetradecyl (phenyltelluro)formate (16) was prepared according to standard protocol (B) in our previously published paper[17] using 1-(benzylseleno)-6-tetradecanol (**12**). Flash chromatography (hexane/ethyl acetate 95:5) afforded **16** as a yellow oil (74%): ^{1}H NMR δ 0.92 (3H, t, J = 6.9 Hz), 1.24−1.42 (22H, m), 2.26 (2H, t, J = 7.5 Hz), 3.53 (2H, s), 5.15 (1H, m), 6.93−7.19 (8H, m), 7.81 (2H, d, J = 7.8 Hz); ^{13}C NMR δ 14.35, 23.05, 23.77, 25.28, 25.81, 26.94, 29.64, 29.77, 29.82, 29.83, 30.32, 32.22, 34.56, 34.75, 79.20, 114.20, 126.75, 128.61, 128.86, 129.22, 129.52, 139.98, 140.13, 156.48; ^{77}Se NMR δ 259.9; ^{125}Te NMR δ 759.9; IR ν (neat) 1709 cm^{-1}; MS m/z (relative intensity) 525 (0.1), 367 (6), 91 (100). Anal. Calcd for $C_{28}H_{40}O_2SeTe$: C, 54.67; H, 6.55. Found: C, 54.32, H, 6.27.

4-Octyl-3-oxaselenan-2-one (18). A 0.15 M solution of 1-(Benzylseleno)-3-undecyl (phenyltelluro)formate (**13**) (103 mg, 180 μmol) in benzene in a water cooled jacket was irradiated with a 250 W low-pressure mercury lamp (white light) at a distance of 20 cm for 64 h. Removal of the solvent in vacuo and preparative TLC (hexane/ethyl acetate 85:15) afforded **18** as a pale oil (37 mg, 73%). ^{1}H NMR δ 0.93 (3H, t, J = 7.2 Hz), 0.99−1.38 (16H, m), 2.05 (1H, m), 2.23 (1H, m), 3.57 (1H, m); ^{13}C NMR δ 14.33, 20.45, 23.05, 24.85, 27.83, 29.60, 29.67, 29.76, 32.23, 35.25, 82.62, 161.73; ^{77}Se NMR δ 307.5; IR ν (neat) 1692 cm^{-1}; MS m/z (relative intensity) 234 (M-CO_2^+, 23), 191 (13), 177 (16), 149 (62), 135 (100). Anal. Calcd for $C_{12}H_{22}O_2Se$: C, 51.98; H, 8.00. Found: C, 52.33, H, 7.99.

1-(*tert*-Butylthio)-3-undecanol. 4-Toluenesulfonyl chloride (2.86 g, 15 mmol) was added to a cooled (0°) solution of undecane-1,3-diol[22] (2.57 g, 13.7 mmol) in dry pyridine and the mixture stored at 4° for 24 h. Ether (100 mL) was added and the resultant solution washed with water (2 × 20 mL), satd $CuSO_4$ (20 mL), 10% HCl (20 mL), and satd $NaHCO_3$ (20 mL). The solution was dried ($MgSO_4$) and the solvent removed in vacuo to afford crude monotosylate **5**. Sodium hydroxide

(26) Haller, W. S.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97.

(850 mg, 20 mmol) and *tert*-butylthiol (480 mg, 5.3 mmol) in DMF (40 mL) was added over a 10 min period to a stirred cooled (0°) solution of **5** (1.5 g, 4.38 mmol) in DMF (20 mL) at which time the solution was stirred at 0° for 5 h and room-temperature overnight. Water (10 mL), 10% HCl (2 mL) and hexane (80 mL) were added, the phases were separated, the organic layer was dried ($MgSO_4$), and the solvent was removed in vacuo. Flash chromatography (hexane/ethyl acetate 80:20) afforded the title compound as a pale oil (230 mg, 20%): ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, J = 6.9 Hz), 1.27−1.45 (14H, m), 1.33 (9H, s), 1.70 (2H, m), 2.09 (1H, d, J = 5.1 Hz), 2.66 (2H, t, J = 7.2 Hz), 3.71 (1H, m); ^{13}C ($CDCl_3$) NMR δ 14.01, 22.57, 24.81, 25.54, 29.18, 29.49, 29.57, 30.85, 31.79, 36.82, 37.49, 41.99, 71.17; IR ν (neat) 3365 cm^{-1}; MS *m*/*z* (relative intensity) 260 (M$^+$, 18), 243 (12), 185 (45), 87 (27), 57 (100). HRMS calcd for $C_{15}H_{32}OS$ 260.4772, found 260.4770.

1-(*tert*-Butylthio)-3-undecyl (phenyltelluro)formate (19) was prepared according to standard protocol (B) in our previously published paper[17] using 1-(*tert*-butylthio)-3-undecanol. Flash chromatography (hexane/ethyl acetate 98:2) aforded **19** as a yellow oil (61%): ^{1}H NMR δ 0.91 (3H, t, J = 6.6 Hz), 1.22 (9H, s), 1.15−1.32 (13H, m), 1.44 (1H, m), 1.65 (1H, m), 1.79 (1H, m), 2.49 (2H, m), 5.29 (1H, m), 6.92−7.03 (3H, m), 7.79 (2H, d, J = 6.9 Hz); ^{13}C NMR δ 14.29, 23.01, 24.69, 25.64, 29.56, 29.65, 29.72, 31.05, 32.18, 34.67, 35.24, 41.86, 78.46, 114.19, 128.86, 129.52, 139.94, 156.18; ^{125}Te NMR δ 760.8; IR ν (neat) 1707 cm^{-1}; MS *m*/*z* (relative intensity) 243 (11), 187 (39), 154 (22), 87 (19), 57 (100). Anal. Calcd for $C_{22}H_{36}O_2STe$: C, 53.69; H, 7.37. Found: C, 53.89, H, 7.43.

2-Octyltetrahydroselenophene (21) was prepared according to standard protocol (F) in our previously published paper[17] using 1-(benzylseleno)-4-dodecyl (phenyltelluro)formate (**14**) in benzene (0.46 M) with heating at 160 °C for 2 d. Preparative TLC (hexane/ethyl acetate 98:2) afforded **21** as a pale oil (87%). ^{1}H NMR δ 0.91 (3H, t, J = 6.9 Hz), 1.24−1.38 (13H, m), 1.63 (3H, m), 1.84 (2H, m), 2.69 (2H, dd, J = 5.4, 7.5 Hz), 3.42 (1H, m); ^{13}C NMR δ 14.33, 23.05, 24.62, 29.67, 29.92, 30.84, 32.25, 32.40, 38.71, 39.93, 45.67; ^{77}Se NMR δ 263.8; MS *m*/*z* (relative intensity) 248 (M$^+$, 25), 191 (8), 177 (14), 135 (25), 83 (100). HRMS calcd for $C_{12}H_{24}{}^{80}Se$ 248.1042, found 248.1039.

2-Octylselenane (22) was prepared according to standard protocol (F) in our previously published paper[17] using 1-(benzylseleno)-5-tridecyl (phenyltelluro)formate (**15**) in benzene (1.05 M) with heating at 160 °C for 12 d. Preparative TLC (hexane/ethyl acetate 98:2) afforded **22** as a pale oil (94%). ^{1}H NMR δ 0.90 (3H, t, J = 6.6 Hz), 1.05−1.66 (18H, m), 1.78−1.92 (2H, m), 2.35 (1H, dt, J = 3.6, 12.3 Hz), 2.56 (1H, dt, J = 2.7, 12.3 Hz), 2.83 (1H, m); ^{13}C NMR δ 14.32, 20.02, 23.05, 27.66, 27.95, 28.32, 29.69, 29.92, 32.25, 36.01, 36.91, 37.63; ^{77}Se NMR δ 237.5; MS *m*/*z* (relative intensity) 262 (M$^+$, 34), 205 (14), 163 (10), 149 (100). HRMS calcd for $C_{13}H_{26}{}^{80}Se$ 262.1199, found 262.1192.

2-Octylselenopane (23) was prepared according to standard protocol (F) in our previously published paper[17] using 1-(benzylseleno)-6-tetradecyl (phenyltelluro)formate (**16**) in benzene (0.79 M) with heating at 160 °C for 20 d. Preparative TLC (hexane/ethyl acetate 98:2) afforded **23** as a pale oil (43%). ^{1}H NMR δ 0.91 (3H, t, J = 6.9 Hz), 1.26−2.00 (22H, m), 2.43 (1H, m), 2.61 (1H, m), 2.85 (1H, m); ^{13}C NMR δ 14.33, 22.95, 23.06, 26.49, 28.17, 28.69, 29.70, 29.94, 29.98, 32.19, 32.25, 38.23, 38.67, 43.04; ^{77}Se NMR δ 230.9; MS *m*/*z* (relative intensity) 275 (M$^+$, 100), 149 (12), 135 (11), 69 (31). Anal. Calcd for $C_{14}H_{28}Se$: C, 61.07; H, 10.26. Found: C, 60.76 H, 9.91.

1-(Benzylseleno)-4-dodecyl (phenylseleno)formate (24) was prepared according to standard protocol (D) in our previously published paper[17] using 1-(benzylseleno)-4-dodecanol (**10**). Flash chromatography (hexane/ethyl acetate 98:2) afforded **24** as a yellow oil (84%). ^{1}H NMR δ 0.91 (3H, t, J = 6.9 Hz), 1.17−1.47 (18H, m), 2.20 (2H, t, J = 6.9 Hz), 3.51 (2H, s), 5.01 (1H, m), 6.98−7.18 (8H, m), 7.57−7.62 (2H, m); ^{13}C NMR δ 14.35, 23.04, 23.51, 25.60, 26.15, 26.97, 29.78, 32.21, 34.52, 79.17, 126.79, 126.95, 128.63, 128.94, 129.20, 129.32, 135.99, 139.97, 166.03; ^{77}Se NMR δ 257.0, 504.5; IR ν (neat) 1721 cm^{-1}; MS *m*/*z* (relative intensity) 540 (M$^+$, 0.92), 405 (1), 339 (40), 247 (19), 91 (100). Anal. Calcd for $C_{26}H_{36}O_2Se_2$: C, 57.99; H, 6.74. Found: C, 58.03; H, 6.70.

1-(Benzylseleno)-4-dodecyl Chloroformate (25). A solution of phosgene in toluene (5.7 M, 1.02 mL, 5.84 mmol) was added to a cooled (0 °C) solution of 1-(benzylseleno)-4-dodecanol (**15**) in THF (10 mL), and the solution was stirred under nitrogen for 90 min. The solvent was removed in vacuo to afford **25** as a yellow oil (218 mg, 89%). ^{1}H NMR δ 0.92 (3H, t, J = 6.9 Hz), 1.09−1.32 (18H, m), 2.15 (2H, m), 3.48 (2H, s), 4.68 (1H, m), 6.98−7.14 (5H, m); ^{13}C NMR δ 14.33, 23.03, 23.26, 25.26, 25.75, 27.05, 29.57, 29.68, 32.18, 33.84, 84.26, 126.87, 128.66, 129.17, 139, 86, 150.19; IR ν (neat) 1760 cm^{-1}; MS *m*/*z* (relative intensity) 418 (M$^+$, 1.9), 374 (2), 247 (28), 91 (100). HRMS calcd for $C_{20}H_{31}O_2{}^{35}Cl^{80}Se$ 418.1305, found 418.1301.

1-(*tert*-Butylthio)-4-dodecyl (phenyltelluro)formate (26) was prepared according to standard protocol (B) in our previously published paper[17] using 1-(*tert*-butylthio)-4-dodecanol. Flash chromatography (hexane/ethyl acetate 98:2) aforded **26** as a yellow oil (68%): ^{1}H NMR δ 0.91 (3H, t, J = 6.9 Hz), 1.16−1.56 (18H, m), 1.22 (9H, s), 2.35 (2H, t, J = 7.2 Hz), 5.17 (1H, m), 6.69−7.02 (3H, m), 7.80 (2H, dd, J = 1.5, 7.5 Hz); ^{13}C NMR δ 14.35, 23.03, 25.74, 26.14, 28.18, 29.60, 29.69, 29.77, 31.13, 32.20, 33.94, 34.71, 41.64, 78.75, 114.21, 128.84, 129.51, 139.95, 156.39; ^{125}Te NMR δ 761.5; IR ν (neat) 1706 cm^{-1}; MS *m*/*z* (relative intensity) 275 (57), 257 (24), 199 (49), 115 (4), 57 (100). Anal. Calcd for $C_{23}H_{38}O_2STe$: C, 54.57; H, 7.57. Found: C, 54.63, H, 7.51.

Thermolysis of 1-(*tert*-butylthio)-4-dodecyl (phenyltelluro)formate (26) (0.46M) was carried out according to standard protocol (D) in our previously published paper[17] at 160 °C for 32 h. Flash chromatography (hexane/ethyl acetate 98:2) afforded 2-octyltetrahydrothiophene (**27**) as a pale oil (43%) contaminated with small amounts of impurities. ^{1}H NMR δ 0.91 (3H, t, J = 7.2 Hz), 1.24−1.35 (14H, m), 1.49−1.77 (4H, m), 2.45 (1H, t, J = 7.5 Hz), 2.65 (1H, m), 3.22 (1H, quin(apparent), J = 7.2 Hz); ^{13}C NMR δ 14.33, 23.05, 29.56, 29.68, 29.93, 30.53, 31.13, 32.07, 32.35, 37.68, 38.26, 49.48; MS *m*/*z* (relative intensity) 201 (73), 154 (19), 87 (26), 77 (86), 28 (100). HRMS calcd for $C_{12}H_{24}S$: 201.1668, found 201.1665. Further elution afforded 1-(*tert*-butylthio)-4-(phenyltelluro)-dodecane (**28**) as a red oil (14%). ^{1}H NMR δ 0.91 (3H, t, J = 6.9 Hz), 1.20−1.30 (10H, m), 1.23 (9H, s), 1.41−1.63 (6H, m), 1.91 (2H, m), 2.45 (1H, m), 2.71 (2H, t, J = 7.5 Hz), 6.94−6.98 (3H, m), 7.72 (2H, dd, J = 1.2, 7.8 Hz); ^{13}C NMR δ 8.57, 14.27, 23.03, 27.13, 29.33, 29.72, 29.98, 30.18, 31.85, 32.27, 37.51, 39.37, 42.72, 42.91, 112.35, 127.28, 129.32, 138.87; ^{125}Te NMR δ 480.5; MS *m*/*z* (relative intensity) 464 (M$^+$, 10), 407 (24), 373 (11), 257 (41), 57 (100). Anal. Calcd for $C_{22}H_{38}STe$: C, 57.17; H, 8.29. Found: C, 57.37, H, 8.41.

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Supporting Information Available: Experimental procedures for the preparation of alcohols **5**−**12** and 1-(*tert*-butylthio)-3-undecanol (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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