(Aryltelluro)formates as Precursors of Alkyl Radicals: Thermolysis and Photolysis of Primary and Secondary Alkyl (Aryltelluro)formates

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Alkyl (aryltelluro)formates are effective precursors of oxyacyl, methyl, and primary and secondary alkyl radicals. At room temperature, irradiation of a benzene solution of methyl (aryltelluro)formates **10**−**12**, 2-methylpropyl (aryltelluro)formates **14** and **15**, octyl (phenyltelluro)formate (**17**), cyclohexyl (aryltelluro)formates **19** and **20**, 3β-cholestanyl (aryltelluro)formates **22** and **23**, cholesteryl (phenyltelluro)formate (**24**) and benzyl (phenyltelluro)formate (**27**) with a 250-W low-pressure mercury lamp leads to the formation of oxyacyl radicals (**34**), which can be trapped by diphenyl diselenide to give the corresponding alkyl (phenylseleno)formates **13**, **16**, **18**, **21**, **24**, **26**, and **28** with excellent overall conversions. Thermolysis of these telluroformates at 160 °C in the dark leads to the formation of methyl and primary and secondary alkyl aryl tellurides **36**−**43** in excellent yields. Presumably, these transformations involve oxyacyl radicals, which undergo subsequent decarboxylation at the elevated temperature to afford alkyl radicals, which become involved in further radical chemistry. When 1-(benzylseleno)-5-hexyl (phenyltelluro)formate (**44**) was thermolysed under these conditions, 2-methylselenane (**45**) was observed as the sole selenium-containing product, demonstrating the synthetic utility of (aryltelluro)formates as alkyl radical precursors.

Introduction

Inter- and intramolecular free-radical homolytic substitution chemistry offers the synthetic chemist a convenient method for the synthesis of a variety of heteroatom-containing organic molecules.[1−9] Intramolecular group transfer and translocation chemistry in molecules containing halo, phenylseleno, trialkylsilyl, and stannyl moieties are representative of processes in which the attacking and leaving radicals form part of the molecule of interest.[2] Intramolecular reactions in which the leaving radical is ejected from the molecule of interest usually result in the formation of higher heterocycles. Recent examples include the attack of alkyl and aryl radicals at the sulfur atom in alkyl sulfides[3] and sulfoxides[4] and the silicon atom in silanes,[5] while we have developed methods for the preparation of selenium-containing heterocycles through the use of free-radical attack of alkyl,[6] aryl,[7] iminyl,[8] and amidyl[9] radicals at the selenium atom in alkyl selenides.

The choice of radical precursor in reactions involving homolytic attack at selenium has proven to be crucial; photolysis or thermolysis of thiohydroxamic esters in the absence of chain carriers is effective in the preparation of saturated selenium-containing heterocycles,[6] while iodides are required in reactions involving tributyltin hydride or tris(trimethylsilyl)silane.[7] Indeed, we demonstrated recently that 2-(benzylseleno)-1-(2-iodophenyl)-ethanol (**1**) reacts with tris(trimethylsilyl)silane to afford benzo[*b*]selenophene, while the analogous bromide **2** affords mainly the selenosilane **3** under identical conditions.[7]

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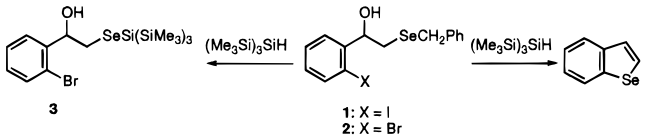
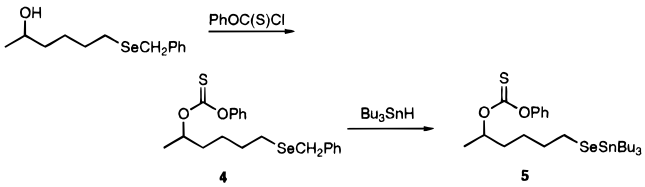


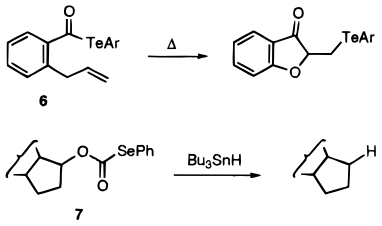
3 1: X = I 2: X = Br

As part of ongoing studies, we required a method for the generation of alkyl radicals from primary and secondary alcohols in the presence of the benzylseleno moiety. Initial work involving the thionoformate functionality as precursor was met with limited success. Thus, 1-(benzylseleno)-5-hexyl (phenyloxy)thionoformate (**4**), prepared under standard conditions,[10] when treated with tributyltin hydride in benzene (AIBN initiator) afforded the stannyl selenide **5** as the sole isolated product of reaction. Clearly, free-radical attack at the thionoformate and subsequent β-scission are not competitive with the homolytic substitution process at selenium.



4 5

Recent high-level *ab initio* calculations performed in our laboratories,[11] together with available rate constant data,[12] suggest that alkyl tellurides react several orders of magnitude more rapidly than alkyl selenides with chain-carrying radicals such as tributylstannyl. In addition, Crich et al. demonstrated recently that acyl tellurides (e.g., **6**) are efficient precursors of acyl radicals which often undergo further radical chemistry.[1c] Several years ago, Pfenniger and co-workers showed that steroidal (phenylseleno)formates (e.g., **7**) react with tributyltin hydride under appropriate conditions to afford decarboxylated products, while Bachi and Bosch demonstrated that oxyacyl radicals derived from selenoformates undergo homolytic addition chemistry.[13]

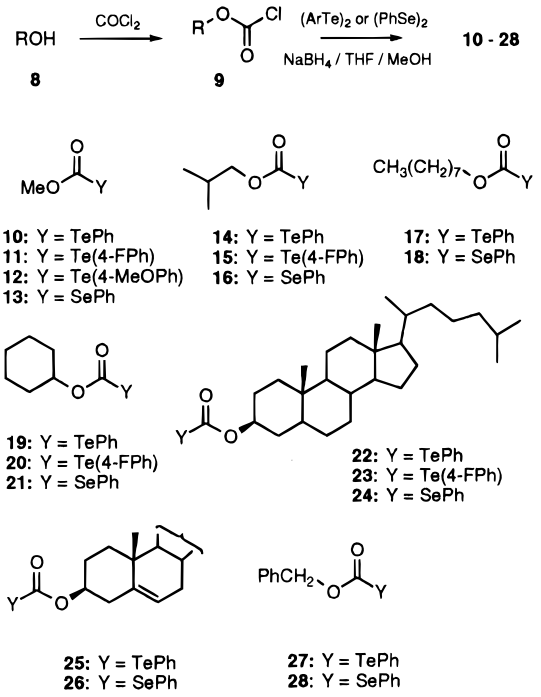


Inspired by these reports, we began to explore the use of (aryltelluro)formates (eq 19) as precursors of carbon-centered radicals. We now report that these telluroformates are photochemically and thermally labile. Under thermolytic conditions, radical formation is accompanied by decarboxylation to afford primary and secondary alkyl radicals, which undergo further reaction to give (aryltelluro)alkanes.

Results and Discussion

Preparation of Telluro- and Selenoformates. (Aryltelluro)formates and (phenylseleno)formates (for authentication of reaction products) were prepared according to the general procedure outlined in Scheme 1. The required alcohol **8** was reacted with a 20% solution of phosgene in toluene to afford the corresponding chloroformate **9**. The chloroformate was not isolated but reacted with sodium aryltelluroate or sodium phenylselenoate, prepared by the reduction of diphenyl ditelluride,[14] bis(4-fluorophenyl) ditelluride,[14] bis(4-methoxyphenyl) ditelluride,[15] or diphenyl diselenide with sodium borohydride in tetrahydrofuran and methanol according to the procedure of Crich et al.[1c] In this manner, the telluro- and selenoformates **10**−**28** were prepared in 60−98% yield.

Scheme 1



There are few examples of the telluroformate functional group in the literature.[16] As such, the chemistry of this novel functional group is largely unexplored. The (aryltelluro)formates prepared in this study are light sensitive and generally range from pale yellow to orange in color. They appear to be stable in the dark at room temperature for indefinite periods and are sufficiently stable on exposure to background light to handle without precaution for short periods.

Photochemical Studies. Given the photochemical lability of aryltelluro esters,[1c] we began to explore the photochemistry of (aryltelluro)formates. Initial studies involved 2-methyl-1-propyl (phenyltelluro)formate (**14**), which was readily prepared from commercially available isobutyl chloroformate. When **14** in benzene-d_6 (0.3 M) in an NMR tube and in a water-cooled jacket was irradiated with a 250-W low-pressure mercury lamp (white light) for 2 d, ^{1}H NMR spectrocopy revealed only starting material (**14**). To confirm that the oxyacyl radical **29** was being formed, the experiment was repeated in the presence of diphenyl diselenide (1 equiv) as a radical trap. ^{1}H NMR spectroscopy indicated the

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Scheme 2

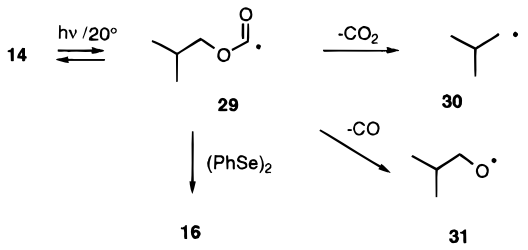

Table 1. Photolysis Half-Lives of (Aryltelluro)formates (0.2 M) in the Presence of Diphenyl Diselenide in Benzene and Selected ^{77}Se and ^{125}Te NMR Data

telluroformate	δ ^{125}Te	product	δ ^{77}Se	half-life (h)
10	771.4	**13**	506.3	15
11	765.3	**13**		19
12	751.9	**13**		20
14	768.9	**16**	505.2	11
15	760.3	**16**		18
17	767.8	**18**	505.6	14
19	771.6	**21**	509.3	9
20	769.9	**21**		11
22	770.2	**24**	509.1	17
23	768.7	**24**		15
25	771.9	**26**	509.8	13
27	784.2	**28**	511.3	6

formation of 2-methyl-1-propyl (phenylseleno)formate (**16**, 90%) after 2 d. This result suggests that radical **29** is being generated on photolysis. In the absence of diphenyl diselenide, decarboxylation to afford the alkyl radical **30** or decarbonylation to afford the alkoxyl radical **31** is not competitive with recombination processes to regenerate the telluroformate **14** (Scheme 2).

The photochemical transformation of **14** to **16** displays the inverse concentration dependence expected for photochemical processes.[17] At 0.37 M concentration, the reaction half-life was determined to be about 15 h by ^{1}H NMR spectroscopy. As the concentration was reduced to 0.25, 0.20, 0.12, and 0.07 M, the half-life was observed to decrease to 13, 11, 8, and 7 h, respectively.

Similar results are obtained for methyl (phenyltelluro)formate (**10**), 1-octyl (phenyltelluro)formate (**17**), cyclohexyl (phenyltelluro)formate (**19**), 3β-cholestanyl (phenyltelluro)formate (**22**), 3β-cholesteryl (phenyltelluro)formate (**25**), and benzyl (phenyltelluro)formate (**27**). Table 1 summarizes the half-life data at 0.2 M for the photochemical reaction of the telluroformates in this study with diphenyl diselenide as well as ^{77}Se and ^{125}Te NMR chemical shifts of the products and reactants, while Figure 1 displays the half-life concentration dependence for a representative set of telluroformates.

Due to their ease of preparation, substituted aryl tellurides are often used as free-radical precursors.[1c,18] Of particular significance has been the use of the 4-fluorophenyl (4-FPh)- and 4-methoxyphenyl (4-MeOPh)-substituted tellurides. To assess the effect of substituents on the progress of these photochemical reactions, several [(4-fluorophenyl)telluro]formates (**11**, **15**, **20**, and **23**) and methyl [(4-methoxyphenyl)telluro]formate (**12**) were reacted under the previously described reaction conditions. As can be seen in Table 1, the effect of both

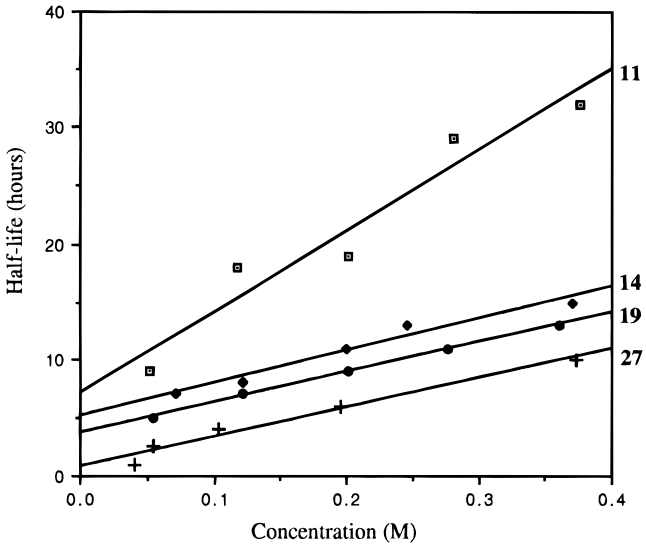

Figure 1. Half-life dependence on concentration for photolysis of (aryltelluro)formates **11**, **14**, **19**, and **27** in the presence of diphenyl diselenide in benzene.

fluoro and methoxy substituents is to increase the reactions half-lives slightly. Only the steroidal system **22** appears to increase in rate with the introduction of fluorine; however, the effect is minor. In our hands, the preparation of diphenyl ditelluride from freshly-prepared phenylmagnesium bromide and tellurium powder presented no difficulties (typical yield, 85%), and it is the reagent of choice for the majority of our work.

Inspection of Table 1 reveals that the ^{125}Te chemical shifts of the (aryltelluro)formates in this study fall between 760 and 785 ppm, while the analogous ^{77}Se shifts associated with the selenoformates were measure to range from 505 to 512 ppm. Reaction half-lives at 0.2 M were measured to be about 15 h for the methyl-substituted (phenyltelluro)formate **10** between 11 and 14 h for the primary alkyl systems **15** and **17**, about 10 h for the (secondary) cyclohexyl (phenyltelluro)formate (**19**), and about 6 h in the case of benzyl (phenyltelluro)formate (**27**), with an inverse dependence on concentration in all cases. Only the steroidal systems **22** and **25** were observed to go against the trend, with slower rates of transformation.

Benzyl (phenyltelluro)formate (**27**) was observed to give products other than the corresponding selenoformate **28** under these photolytic conditions. The ^{1}H NMR spectrum of the reaction mixture obtained after **27** (0.04 M) was irradiated for 24 h revealed the presence of benzyl (phenylseleno)formate (**28**), benzyl phenyl selenide[19] (**32**), and benzyl formate (**33**) in approximately equal quantities by comparison with authentic samples. While **28** presumably arises by reaction of the intermediate oxyacyl radical with diphenyl diselenide, the presence of **33** clearly indicates that decarboxylation to afford the stable benzyl radical and subsequent reaction with diphenyl diselenide is competitive in this case. The formate **33** presumably arises through hydrogen abstraction by the oxyacyl radical from a reactive benzylic position. Interestingly, formates are not observed in the remaining examples in this study.

Ingold, Lusztyk, and co-workers recently reported[20] that acyl radicals are less reactive than their alkyl

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counterparts and appear to be resonance stabilized, a phenomenon which is readily observable in the infrared spectra of the radicals in question. Acyl radicals, therefore, appear not to be the highly reactive species normally associated with σ-radicals. With this in mind, we speculate that the photolytic reactivities reported in Table 1 are the result of hyperconjugative contributions by the alkyl group to the overall structure of **34**. Resonance contributor **35** becomes more important as the alkyl radical (R•) is stabilized by hyperconjugation or, in the case of benzyl, by resonance.

In our laboratories, ^{77}Se and ^{125}Te NMR spectroscopy is routinely used to assess the outcome of reactions involving selenium- and tellurium-containing compounds. The ^{77}Se NMR spectrum of the reaction mixture obtained after the photolysis of any of the telluroformates in this study in the presence of diphenyl diselenide displays a single signal in the range δ 505−512 as well as a single signal in the range δ 261−287 (diphenyl diselenide at δ 464 is also observed). The former signal was shown to correspond to the product (phenylseleno)formate by comparision with an authentic sample, while the latter was assigned to the dichalcogenide cross-product (PhSeTeAr). ^{125}Te NMR spectroscopy revealed a signal in the range δ 836−847 for this dichalcogenide.

To confirm the presence of the selenotelluride in the reaction mixture, an equimolar mixture of diphenyl diselenide and diphenyl ditelluride was dissolved in benzene. ^{77}Se and ^{125}Te NMR spectroscopy revealed the presence of PhSeTePh (^{77}Se, δ 264; ^{125}Te, δ 837) in addition to diphenyl diselenide and diphenyl ditelluride. It is well established that solutions of diselenides and ditellurides undergo rapid statistical chalcogen scrambling.[21] Similar experiments involving bis(4-fluorophenyl) ditelluride and bis(4-methoxyphenyl) ditelluride confirmed the presence the respective dichalcogenide (PhSeTeAr) in reactions involving the (4-fluorophenyl)- and [(4-methoxyphenyl)telluro]formates, respectively.[22]

In accordance with the mechanism proposed by Crich et al. for telluro esters,[1c] it seems reasonable to suggest that the telluroformates in this study are involved in a chain mechanism in which homolytic substitution by phenylseleno radicals at the tellurium atom in the telluroformate plays an important role (Scheme 3). The formation of the selenotelluride is a consequence of this mechanism; its formation, however, can also be explained on the basis of direct attack of the aryltelluro radical, generated in the primary photolytic process, at diphenyl diselenide.

Thermal Studies. Having demonstrated that the radicals **34** in this study generally fail to decarboxylate or decarbonylate at room temperature, we set out to explore the conditions under which these telluroformates are effective as alkyl radical precursors. Once again, 2-methyl-1-propyl (phenyltelluro)formate (**14**) was chosen as our initial substrate. When **14** in benzene-d_6 (0.3 M) in an NMR tube was heated at 80° (shielded from background light) for 2 d, ^{1}H NMR spectrocopy revealed only starting material **14**. In the presence of diphenyl diselenide, 35% conversion to the selenoformate **16** was observed after thermolysis for 22 d. It would appear that the radical **29** is being generated under these thermolytic

Scheme 3

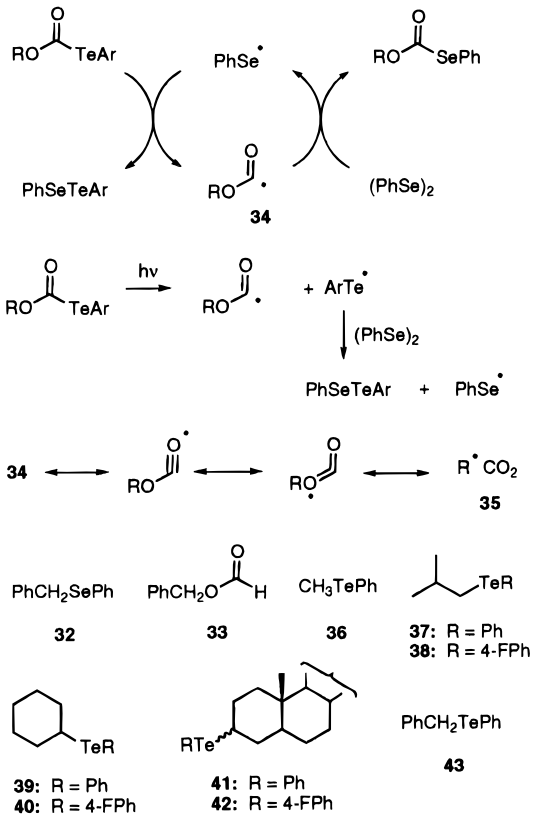


Table 2. Thermolysis Half-Lives of (Aryltelluro)formates (0.2 M) in Benzene at 160 °C and Selected Product ^{125}Te NMR Data

telluroformate	product	δ ^{125}Te	half-life
10	**36**[a]	337.4	33 d
14	**37**[a]	421.2	19 d
15	**38**	423.6	12 d
19	**39**[b]	nd[e]	6 d
20	**40**	nd[e]	6 d
22	**41**[c]	677.8, 591.4	11 d
23	**42**	674.2, 589.2	10 d
27	**43**[d]	679.2	8 h

[a] Reference 28. [b] Reference 23. [c] Reference 29. [d] Reference 24. [e] Not determined, see text.

conditions; however, decarboxylation or decarbonylation would, once again, appear not to be competitive processes. Pfenniger and co-workers report that temperatures of 140−160° are required for decarboxylation of oxyacyl radicals derived from steroidal selenoformates.[13] With this in mind, the telluroformate **14** in benzene-d_6 (0.2 M) in a sealed NMR tube was heated at 160°. ^{1}H NMR spectrocopy revealed starting material **14** and 2-methyl-1-(phenyltelluro)propane (**37**) in approximately equal proportions after 19 d. The reaction appears to be extremely clean, with smooth formation of the decarboxylated product under these conditions. When the reaction was repeated using cyclohexyl (phenyltelluro)-formate (**19**) as a representative secondary system at 0.2 M, the reaction half-life was determined to be about 6 d by ^{1}H NMR spectroscopy. Table 2 lists the reaction half-lives for a representative set of (aryltelluro)formates along with product ^{125}Te NMR chemical shifts, which were found to lie between 340 and 680 ppm, depending on the alkyl substituent. We were unable to obtain a ^{125}Te signal for either of the (aryltelluro)cyclohexanes **39** and **40**, presumably due to problems associated with ring inversion.[23]

(21) McFarlane, H. C. E.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1973**, 2416.

(22) Measured NMR data. (4-FPh)TeSePh: ^{77}Se δ 280.2; ^{125}Te δ 847.1. (4-MeOPh)TeSePh: ^{77}Se δ 286.5; ^{125}Te δ 846.7.

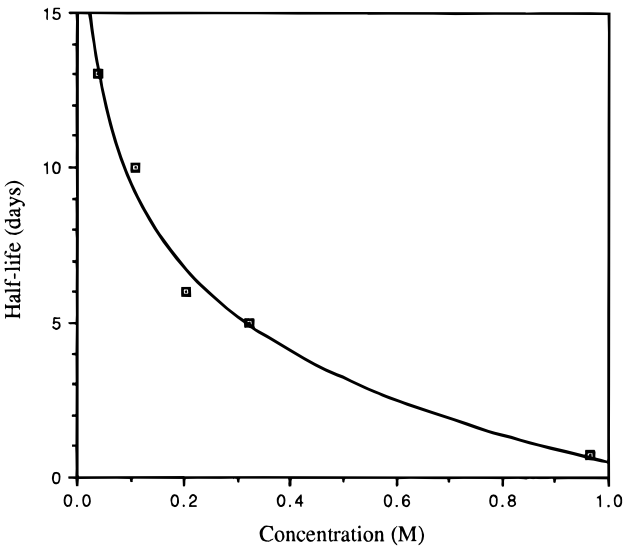


Figure 2. Half-life dependence on concentration for thermolysis of cyclohexyl (phenyltelluro)formate (**19**) at 160 °C in benzene.

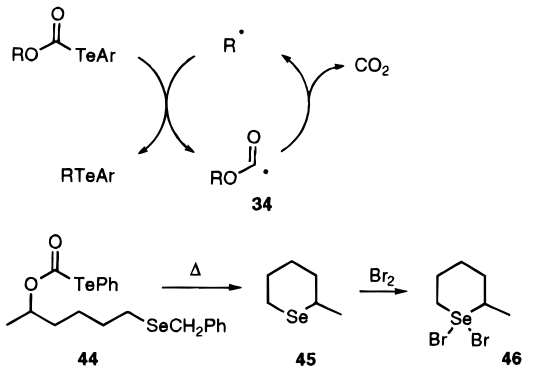
Methyl (phenyltelluro)formate (**10**), 3β-cholestanyl (phenyltelluro)formate (**22**), and benzyl (phenyltelluro)-formate (**27**) were determined to have half-lives of 33 d, 11 d, and 8 h, respectively. The introduction of fluorine (**15**, **20**, and **23**) appears to have only a marginal effect on the rate of reaction (Table 2). All telluroformates appear to decarboxylate smoothly at 160° to afford the corresponding alkyl aryl tellurides **36**−**42**, with the exception of the benzyl system **27**, which appeared to produce substantial quantities of biphenyl and diphenyl ditelluride in addition to benzyl phenyl telluride (**43**). This is not surprising, as **43** is known to decompose readily.[24] The observed substrate reactivities are in accord with those expected on the basis of the nature of the intermediate alkyl radical.

3β-Cholestanyl (phenyltelluro)formate (**22**) and the fluorinated derivative **23** yielded the corresponding 3-aryltellurocholestanes[25] **41** and **43** as an epimeric mixture (α:$\beta \approx$ 1:3.5), which is not surprising, given that the intermediate 3-cholestanyl radical has two distinct faces for attack.

The thermolytic transformation of telluroformate into alkyl telluride displays the expected concentration dependence. We chose to explore this concentration dependence for the reaction involving cyclohexyl (phenyltelluro)formate (**19**). At 160°, the reaction half-life varied from 13 d (0.04 M) to 17 h (0.96 M) (Figure 2). These data suggest that concentrations greater than about 0.5 M are required for synthetically viable reactions.

To test the synthetic viability of these telluroformates as radical precursors, tellurides **39** and **41** were prepared from the corresponding telluroformates **19** and **22**. Thus, cyclohexyl (phenyltelluro)formate (**19**) in benzene (1.0 M) was heated in a sealed tube at 160° for 7 d. Solvent evaporation and chromatography afforded (phenyltelluro)cyclohexane (**39**) in 85% yield. In similar fashion,

Scheme 4



3β-cholestanyl (phenyltelluro)formate (**22**, 1.6 M) was transformed into the epimeric mixture of **41** in 71% yield (92% based on recovered starting material).[25]

Finally, we reacted 1-(benzylseleno)-5-hexyl (phenyltelluro)formate (**44**, 0.7 M) under these conditions. To our delight, ^{1}H NMR spectroscopy indicated the quantitative formation of benzyl phenyl telluride (**43**) and 2-methylselenane[26] (**45**), which was isolated as the dibromide[26] **46** in 74% yield.

Conclusions

By controlling the reaction conditions, alkyl (aryltelluro)formates can be employed as precursors of oxyacyl or alkyl radicals. Photolysis at room temperature leads to the formation of the oxyacyl radicals, which can be trapped by diphenyl diselenide, while thermolysis at 160° can be used as a method for the generation of methyl and primary and secondary alkyl radicals, which become involved in further radical chemistry. The synthetic utility of (aryltelluro)formates as alkyl radical precursors is demonstrated in the transformation of 1-(benzylseleno)-5-hexyl (phenyltelluro)formate (**44**) into 2-methylselenane (**45**).

Experimental Section

Diphenyl ditelluride, bis(4-fluorophenyl) ditelluride, and bis(4-methoxyphenyl) ditelluride were prepared according to published procedures.[14,15] Diphenyl diselenide was purchased from Fluka and used without further purification. Phosgene was purchased from Fluka as a 20% solution in toluene (1.93 M). 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.

Standard Protocol (A) for the Preparation of (Aryltelluro)formates from Chloroformates. Methyl (Phenyltelluro)formate (10). Sodium borohydride (113 mg, 3.0 mmol) was added with stirring to a solution of diphenyl ditelluride (420 mg, 1.0 mmol) in THF (30 mL). The reaction vessel was purged with nitrogen, and methanol (~250 μL) was added dropwise until the red solution turned colorless (30 min). When the evolution of hydrogen had ceased (~60 min), methyl chloroformate (208 mg, 2.2 mmol) was added via syringe, and the resulting mixture was stirred for a further 60 min. Water (10 mL) was added, and the mixture was extracted into ether (3 × 50 mL). The combined ether extracts were dried ($MgSO_4$), and the solvent was removed *in vacuo* to afford a yellow oil. Pure **10** (480 mg, 91%) was obtained after Kügelrohr distillation (50−60°/0.075 mmHg): ^{1}H NMR δ 3.27 (3H, s), 6.95−7.12 (3H, m), 7.74−7.77 (2H, m); ^{13}C NMR δ 53.64, 113.76, 128.96, 129.58, 139.96, 156.78; ^{125}Te NMR δ 771.4; IR ν (C=O) (neat) 1711 cm^{-1}; MS *m*/*z* (relative intensity) 266 (M^+, 10.1),

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(24) Comasseto, J. V.; Ferreira, J. T. B.; Fontanillas Val, J. A. *J. Organomet. Chem.* **1984**, *277*, 261.

(25) 3α-(Phenyltelluro)cholestane has been reported previously: Clive, D. L. J.; Chittattu, G. J.; Farina, V.; Kiel, W. A.; Menchen, S. M.; Russell, C. G.; Singh, A.; Wong, C. K.; Curtis, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 4438.

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222 (3), 207 (34), 92 (24), 77 (100). Anal. Calcd for $C_8H_8O_2Te$: C, 36.43; H, 3.06. Found: C, 36.39; H, 3.10.

Methyl [(4-fluorophenyl)telluro]formate (**11**) was prepared according to the standard protocol (A) using bis(4-fluorophenyl) ditelluride and methyl chloroformate. Kügelrohr distillation (50−60° /0.075 mmHg) afforded **11** as a yellow oil (93%): ^{1}H NMR δ 3.27 (3H, s), 6.56−6.62 (2H, m), 7.47−7.51 (2H, m); ^{13}C NMR δ 53.75, 107.70, 116.92 (d, J= 20.7 Hz), 142.34 (d, J = 8.1 Hz), 156.82, 163.74 (d, J = 247.7 Hz); ^{125}Te NMR δ 765.3; IR ν (C=O) (neat) 1711 cm^{-1}; MS *m*/*z* (relative intensity) 283 (M$^+$, 21.5), 225 (61), 239 (8), 130 (9), 95 (100); HRMS calcd for $C_8H_7O_2TeF$ 282.9421, found 282.9426.

Methyl [(4-methoxyphenyl)telluro]formate (**12**) was prepared according to the standard protocol (A) using bis(4-methoxyphenyl) ditelluride and methyl chloroformate. Recrystallization from ethanol gave a light brown, low melting solid (87%): ^{1}H NMR δ 3.16 (3H, s), 3.27 (3H, s), 6.58 (2H, d, *J* = 9 Hz), 7.71 (2H, d, *J* = 9 Hz); ^{13}C NMR δ 53.55, 54.57, 103.23, 115.73, 142.28, 160.95; ^{125}Te NMR δ 751.9; IR ν (C=O) (neat) 1712 cm^{-1}; MS *m*/*z* (relative intensity) 296 (M$^+$, 33.0), 237 (100), 222 (31), 167 (4), 122 (35). Anal. Calcd for $C_9H_{10}O_3Te$: C, 36.80; H, 3.43. Found; C, 36.76; H, 3.38.

2-Methyl-1-propyl (phenyltelluro)formate (**14**) was prepared according to the standard protocol (A) using diphenyl ditelluride and isobutyl chloroformate. Kügelrohr distillation (60−70°/0.08 mmHg) afforded **14** as a yellow oil (86%): ^{1}H NMR δ 0.60 (6H, d, *J* = 6.9 Hz), 1.58 (1H, m), 3.82 (2H, d, *J* = 6.6 Hz), 6.95−7.05 (3H, m), 7.78−7.81 (2H, m); ^{13}C NMR δ 18.78, 28.05, 73.64, 113.97, 128.90, 129.53, 140.07, 156.45; ^{125}Te NMR δ 768.9; IR ν (C=O) (neat) 1709 cm^{-1}; MS *m*/*z* (relative intensity) 308 (M$^+$, 3.6), 284 (0.2), 208 (12), 77 (48), 56 (100). Anal. Calcd for $C_{11}H_{14}O_2Te$: C, 43.20; H, 4.61. Found; C, 43.03; H, 4.70.

2-Methylpropyl [(4-fluorophenyl)telluro]formate (**15**) was prepared according to the standard protocol (A) using bis-(4-fluorophenyl) ditelluride and isobutyl chloroformate. Kügelrohr distillation (60−70°/0.075 mmHg) afforded **15** as a yellow oil (83%): ^{1}H NMR δ 0.61 (6H, d, *J* = 6.9 Hz), 1.59 (1H, m), 3.83 (2H, d, *J* = 6.6 Hz), 6.58−6.64 (2H, m), 7.51−7.56 (2H, m); ^{13}C NMR δ 18.75, 28.05, 73.76, 107.99, 116.90 (d, *J* = 21.2 Hz), 142.42 (d, *J* = 7.6 Hz), 156.45, 163.71 (d, *J* = 248.3 Hz); ^{125}Te NMR δ 760.3; IR ν (C=O) (neat) 1711 cm^{-1}; MS *m*/*z* (relative intensity) 325 (M$^+$, 3.1), 225 (17), 130 (5), 95 (36), 56 (100); HRMS calcd for $C_{11}H_{13}O_2TeF$ 324.9891, found 324.9898.

Standard Protocol (B) for the Preparation of Telluroformates from Alcohols. Cyclohexyl (Phenyltelluro)formate (19). Sodium borohydride (261 mg, 6.9 mmol) was added with stirring to a solution of diphenyl ditelluride (930 mg, 2.3 mmol) in THF (50 mL). The reaction vessel was purged with nitrogen, and methanol (∼250 μL) was added dropwise until the red solution turned colorless (30 min). In a separate reaction vessel, 20% phosgene solution (15 mL, 29 mmol) was added via syringe to a solution of cyclohexanol (500 mg, 5.0 mmol) in THF (50 mL) under nitrogen. The solution was stirred for a further 60 min and concentrated *in vacuo* to approximately half the original volume. After purging with nitrogen, the solution of the chloroformate was transferred via cannula into the solution containing the sodium phenyltelluroate, and the resulting light yellow solution was stirred at room temperature under nitrogen overnight. Water (10 mL) was added, and the mixture was extracted with ether (3 × 50 mL). The combined ether extracts were dried ($MgSO_4$), and the solvent was removed *in vacuo*. The telluroformate **19** was obtained as a yellow oil after flash chromatogaphy (hexane/ethyl acetate 99:1) (1.35 g, 90%): ^{1}H NMR δ 0.93−1.63 (10H, m), 4.95 (1H, m), 6.93−7.02 (3H, m), 7.80−7.83 (2H, m); ^{13}C NMR δ 23.52, 25.32, 31.84, 77.09, 114.32, 128.82, 129.50, 139.95, 155.81; ^{125}Te NMR δ 771.6; IR ν (C=O) (neat) 1709 cm^{-1}; MS *m*/*z* (relative intensity) 333 (M$^+$, 0.5), 289 (0.7), 208 (7), 130 (1), 83 (100). Anal. Calcd for $C_{13}H_{16}O_2Te$: C, 47.05, H, 4.86. Found C, 46.93, H, 4.96.

1-Octyl (phenyltelluro)formate (**17**) was prepared according to the standard protocol (B) using diphenyl ditelluride and 1-octanol. Flash chromatography (hexane/ethyl acetate 98:2) afforded **17** as a yellow oil (98%): ^{1}H NMR δ 0.89 (3H, t, *J* = 7.2 Hz), 1.03−1.38 (12H,m), 4.03 (2H, t, *J* = 6.9 Hz), 6.95−7.04 (3H, m), 7.95−7.80 (2H, m); ^{13}C NMR δ 14.32, 23.00, 25.99, 28.98, 29.34, 29.43, 32.07, 67.98, 114.01, 128.90, 129.54, 140.01, 156.51; ^{125}Te NMR δ 767.8; IR ν (C=O) (neat) 1716 cm^{-1}; MS *m*/*z* (relative intensity) 364 (M$^+$, 1.8), 320 (0.50), 284 (2), 154 (8.0), 56 (100); HRMS calcd for $C_{15}H_{22}O_2Te$ 364.0689, found 364.0678.

Cyclohexyl [(4-fluorophenyl)telluro]formate (**20**) was prepared according to the standard protocol (B) using bis(4-fluorophenyl) ditelluride and cyclohexanol. Flash chromatography (hexane/ethyl acetate 99:1) afforded **20** as a yellow oil (73%): ^{1}H NMR δ 0.92−1.62 (10H, m), 4.94 (1H, m), 6.60 (2H, m), 7.55 (2H, m); ^{13}C NMR δ 23.52, 25.27, 31.84, 77.30, 108.27 (d, *J* = 3.5 Hz), 116.88 (d, *J* = 20.8 Hz), 142.33 (d, *J* = 7.6 Hz), 155.84, 163.70 (d, *J* = 247.7 Hz); ^{125}Te NMR δ 769.9; IR ν (C=O) (neat) 1709 cm^{-1}; MS *m*/*z* (relative intensity) 352 (M$^+$, 0.3), 225 (11), 220 (3), 95 (25), 83 (100). Anal. Calcd for $C_{13}H_{15}O_2TeF$: C, 44.62; H, 4.32. Found: C, 44.65; H, 4.38.

3β-Cholestanyl (phenyltelluro)formate (**22**) was prepared according to the standard protocol (B) using diphenyl ditelluride and 3β-cholestanol. Recrystallization from ethanol gave **22** as a white solid (70%): mp = 126−127°; ^{1}H NMR δ 0.35−1.98 (46H, m), 4.97 (1H, m), 6.96−7.02 (3H, m), 7.84−7.87 (2H, m); ^{13}C NMR δ 12.12, 12.30, 19.00, 21.43, 22.77, 23.03, 24.33, 24.50, 28.01, 28.40, 28.63, 28.68, 32.13, 34.54, 35.38, 35.56, 36.20, 36.64, 36.78, 39.91, 40.34, 42.83, 44.56, 54.17, 56.66, 78.34, 114.32, 128.86, 129.58, 139.90, 156.03; ^{125}Te NMR δ 770.2; IR ν (nujol) (C=O) 1710 cm^{-1}; MS *m*/*z* (relative intensity) 578 (14.4), 409 (3), 371 (69), 245 (10), 95 (100), 81 (82). Anal. Calcd for $C_{34}H_{52}O_2Te$: C, 65.83; H, 8.45. Found: C, 65.91, H, 8.52.

3β-Cholestanyl [(4-fluorophenyl)telluro]formate (**23**) was prepared according to the standard protocol (B) using bis-(4-fluorophenyl) ditelluride and 3β-cholestanol. Recrystallization from ethanol gave **23** as a white solid (75%): mp = 113.5−114.5°; ^{1}H NMR δ 0.38−1.99 (46H, m), 4.97 (1H, m), 6.62 (2H, m), 7.59 (2H, m); ^{13}C NMR δ 12.13, 12.30, 19.00, 21.44, 22.76, 23.03, 24.33, 24.50, 28.02, 28.40, 28.62, 28.68, 32.13, 34.56, 35.38, 35.56, 36.20, 36.64, 36.78, 39.91, 40.33, 42.84, 44.57, 54.18, 56.62, 56.66, 78.58, 108.30, 116.95 (d, *J* = 21.2 Hz), 142.24 (d, *J* = 7.6 Hz), 155.98, 163.72 (d, *J* = 247.2 Hz); ^{125}Te NMR δ 768.7; IR ν (C=O) 1717 cm^{-1}; MS *m*/*z* (relative intensity) 578 (0.35), 495 (6), 370 (36), 316 (14), 203 (10), 81 (100). Anal. Calcd for $C_{34}H_{51}O_2TeF$: C, 63.97; H, 8.05. Found: C, 63.93; H 8.29.

3β-Cholesteryl [(4-fluorophenyl)telluro]formate (**25**) was prepared according to the standard protocol (B) using diphenyl ditelluride and cholesterol. Recrystallization from ethanol afforded **25** as a white solid (80%): mp = 127−128°; ^{1}H NMR δ 0.64−2.48 (43H, m), 4.98 (1H, m), 5.25 (1H, m), 6.95−7.05 (3H, m), 7.82−7.86 (2H, m); ^{13}C NMR δ 12.03, 19.04, 19.23, 21.26, 22.79, 23.05, 24.35, 24.56, 28.29, 28.40, 28.60, 32.03, 32.21, 36.19, 36.64, 37.07, 38.69, 39.91, 40.07, 42.53, 50.13, 56.49, 56.88, 74.25, 78.52, 114.29, 123.17, 128.88, 129.58, 139.41, 139.88, 155.91; ^{125}Te NMR δ 771.9; IR ν (Nujol) (C=O) 1717 cm^{-1}; MS *m*/*z* (relative intensity) (21 eV) 575 (1.7), 369 (100), 284, (4), 207 (17), 175 (14), 161 (34). Anal. Calcd for $C_{34}H_{50}O_2Te$: C, 66.04; H, 8.15. Found: C, 66.16; H 7.98.

Benzyl (phenyltelluro)formate (**27**) was prepared according to the standard protocol (B) using diphenyl ditelluride and benzyl alcohol. Flash chromatography (hexane/ethyl acetate 98:2) afforded **27** as an orange oil (60%); ^{1}H NMR δ 4.96 (2H, s), 6.94−7.02 (8H, m), 7.73−7.75 (2H, m); ^{13}C NMR δ 69.23, 113.95, 128.51, 128.64, 128.71, 128.96, 129.56, 135.66, 140.01, 156.45; ^{125}Te NMR δ 784.2; IR ν (neat) (C=O) 1709 cm^{-1}; MS *m*/*z* (relative intensity) 342 (M$^+$, 0.94), 298 (3), 207 (16), 91 (100), 77 (61); HRMS calcd for $C_{14}H_{12}O_2Te$ 341.9907, found 341.9922.

Standard Protocol (C) for the Preparation of (Phenylseleno)formates from Chloroformates. Methyl (Phenylseleno)formate (13). Sodium borohydride (148 mg, 3.9 mmol) was added with stirring to a solution of diphenyl diselenide (400 mg, 1.3 mmol) in THF (30 mL). The reaction vessel was purged with nitrogen, and methanol (∼250 μL) was added dropwise until the yellow solution turned colorless (30 min). When the evolution of hydrogen had ceased (∼60 min), methyl chloroformate (265 mg, 2.8 mmol) was added via

syringe, and the resulting mixture was stirred for a further 2 h. Water (10 mL) was added, and the mixture was extracted into ether (3 × 50 mL). The combined ether extracts were dried ($MgSO_4$), and the solvent was removed *in vacuo* to afford a yellow oil. Pure **13** (483 mg, 88%) was obtained as a pale oil after Kügelrohr distillation (40−50°/0.075 mmHg): ^{1}H NMR δ 3.22 (3H, s), 6.96−6.98 (3H, m), 7.53−7.54 (2H, m); ^{13}C NMR δ 54.15, 129.05, 129.36, 135.95, 166.62; ^{77}Se NMR δ 506.3; IR ν (C=O) (neat) 1724 cm^{-1}; MS *m*/*z* (relative intensity) 216 (M^+, 30.3), 172 (23), 157 (100), 91 (33), 77 (66). Anal. Calcd for $C_8H_8O_2Se$: C, 44.67; H, 3.75. Found: C, 44.60; H, 3.82.

2-Methyl-1-propyl (phenylseleno)formate (**16**) was prepared according to the standard protocol (C) using diphenyl diselenide and isobutyl chloroformate. Kügelrohr distillation (40−50°/0.075 mmHg) gave a pale yellow oil (85%): ^{1}H NMR δ 0.91 (6H, d, J = 6.6 Hz), 1.96 (1H, m), 4.04 (2H, d, J = 6.6 Hz), 7.34−7.38 (3H, m), 7.61−7.63 (2H, m); ^{13}C NMR δ 18.85, 27.86, 74.17, 119.94, 128.99, 129.18, 135.75, 166.80; ^{77}Se NMR δ 505.2; IR ν (C=O) (neat) 1726 cm^{-1}. Anal. Calcd for $C_{11}H_{14}O_2Se$: C, 51.37; H, 5.49. Found: C, 51.30; H, 5.47.

Standard Protocol (D) for the Preparation of Selenoformates from Alcohols. Cyclohexyl (Phenylseleno)formate (21). Sodium borohydride (182 mg, 4.8 mmol) was added with stirring to a solution of diphenyl diselenide (500 mg, 1.6 mmol) in THF (50 mL). The reaction vessel was purged with nitrogen, and methanol (~250 μL) was added dropwise until the red solution turned colorless (30 min). In a separate reaction vessel, 20% phosgene solution (15 mL, 29 mmol) was added via syringe to a solution of cyclohexanol (353 mg, 3.5 mmol) in THF (50 mL) under nitrogen. The solution was stirred for a further 60 min and concentrated *in vacuo* to approximately half the original volume. After purging with nitrogen, the solution of the chloroformate was transferred via cannula into the solution containing the sodium phenylselenoate, and the resulting colorless solution was stirred at room temperature under nitrogen overnight. Water (10 mL) was added, and the mixture was extracted with ether (3 × 50 mL). The combined ether extracts were dried ($MgSO_4$), and the solvent was removed *in vacuo*. The selenoformate **21** was obtained as a yellow oil after flash chromatogaphy (hexane/ethyl acetate 99:1) (878 mg, 97%): ^{1}H NMR δ 0.92−1.65 (10H, m), 4.87 (1H, m), 6.99−7.01 (3H, m), 7.60−7.63 (2H, m); ^{13}C NMR δ 23.48, 25.28, 31.63, 77.48, 120.35, 128.94, 129.31, 136.00, 165.44; ^{77}Se NMR δ 509.3; IR ν (C=O) (neat) 1727 cm^{-1}; MS *m*/*z* (relative intensity) 238 (2.7), 197 (7), 158 (7), 105 (7), 83 (100). Anal. Calcd for $C_{13}H_{16}O_2Se$: C, 55.13; H, 5.69. Found: C, 54.95; H, 5.61.

1-Octyl (phenylseleno)formate (**18**) was prepared according to the standard protocol (D) using diphenyl diselenide and 1-octanol. Flash chromatography (hexane/ethyl acetate 99:1) afforded **18** as a yellow oil (70%): ^{1}H NMR δ 0.89 (3H, t, J = 6.9 Hz), 1.03−1.38 (12H, m), 3.99 (2H, t, J = 6.6 Hz), 6.98−7.00 (3H, m), 7.58−7.61 (2H, m); ^{13}C NMR δ 14.32, 22.99, 25.92, 28.88, 29.35, 29.42, 32.07, 68.42, 126.77, 128.98, 129.34, 136.03, 166.19; ^{77}Se NMR δ 505.6; IR ν (C=O) (neat) 1726 cm^{-1}; MS *m*/*z* (relative intensity) 314 (M^+, 4.2), 236 (0.9), 185 (2), 171 (0.7), 158 (100), 117 (6). Anal. Calcd for $C_{15}H_{22}O_2Se$: C, 57.51; H, 7.08. Found: C, 57.53; H, 7.26.

3β-Cholestanyl (phenylseleno)formate (**24**) was prepared according to the standard protocol (D) using diphenyl diselenide and 3β-cholestanol. Recrystallization from ethanol afforded **24** as a white solid (72%): mp = 138−139°; ^{1}H NMR δ 0.58−1.98 (46H, m), 4.89 (1H, m), 7.01−7.03 (3H, m), 7.64−7.66 (2H, m); ^{13}C NMR δ 12.14, 12.32, 19.02, 21.46, 22.79, 23.05, 24.36, 24.52, 27.83, 28.41, 28.64, 28.70, 32.15, 34.34, 35.40, 35.58, 36.21, 36.66, 36.76, 36.93, 40.36, 42.85, 44.54, 54.20, 56.65, 56.68, 78.70, 127.11, 128.92, 129.35, 136.00, 165.61; ^{77}Se NMR δ 509.1; IR ν (C=O) (neat) 1719 cm^{-1}; MS *m*/*z* (relative intensity) 528 (5.3), 371 (47), 316 (14), 301 (5), 203 (16), 56 (100). Anal. Calcd for $C_{34}H_{52}O_2Se$: C, 71.43; H, 9.17. Found: C, 71.44; H, 8.94.

3β-Cholesteryl (phenylseleno)formate (**26**) was prepared according to the standard protocol (D) using diphenyl diselenide and cholesterol. Recrystallization from ethanol afforded **26** as a white solid (91%): mp = 135−136°; ^{1}H NMR δ 0.64−2.49 (43H, m), 4.89 (1H, m), 5.25 (1H, m), 7.00−7.03 (3H, m), 7.63−7.66 (2H, m); ^{13}C NMR δ 12.03, 19.03, 19.21, 21.25, 22.77, 23.03, 24.34, 24.55, 28.10, 28.39, 28.59, 32.02, 32.20, 36.18, 36.63, 36.99, 38.48, 39.91, 40.07, 42.53, 50.12, 56.49, 56.88, 78.85, 123.22, 126.99, 128.96, 129.36, 136.00, 139.31, 165.59; ^{77}Se NMR δ 509.8; IR ν (Nujol) (C=O) 1720 cm^{-1}; MS *m*/*z* (relative intensity) 525 (1.6), 369 (100), 247 (8), 215 (6), 187 (3), 161 (20). Anal. Calcd for C_{34} H_{50} O_2 Se: C, 71.68; H, 8.85. Found: C, 71.24; H, 8.96.

Benzyl (phenylseleno)formate (**28**) was prepared according to the standard protocol (D) using diphenyl diselenide and benzyl alcohol. Vaccum chromatography (hexane/ethyl acetate 90:10) afforded pure **19** as a light yellow oil (90%), which solidified on standing: mp = 39−40°; ^{1}H NMR δ 4.92 (2H, s), 6.96−7.05 (8H, m), 7.51−7.55 (2H, m); ^{13}C NMR δ 69.65, 126.54, 128.58, 128.67, 128.71, 129.05, 129.35, 135.45, 136.04, 166.27; ^{77}Se NMR δ 511.3; IR ν (C=O) (neat) 1714 cm^{-1}; MS *m*/*z* (relative intensity) 248 (2.8), 157 (6), 105 (3), 91 (100), 77(13), 65 (13); HRMS calcd for $C_{13}H_{12}Se$ 248.0104, found 248.0100.

Standard Protocol (E) for the Formation of Alkyl Aryl Tellurides. 1-(4-Fluorophenyl)-2-methylpropane (38). Sodium borohydride (128 mg, 3.4 mmol) was added with stirring to a solution of bis(4-fluorophenyl) ditelluride (500 mg, 1.1 mmol) in THF (40 mL). The reaction vessel was purged with nitrogen and methanol (~200 μL) was added dropwise until the red solution turned colorless (30 min). When the evolution of hydrogen had ceased (~60 min), 1-bromo-2-methylpropane (339 mg, 2.5 mmol) was added via syringe, and the resulting mixture was stirred for a further 60 min. Water (10 mL) was added, and the mixture was extracted into ether (3 × 50 mL). The combined ether extracts were dried ($MgSO_4$), and the solvent was removed *in vacuo* to afford a yellow oil. The telluride **38** (480 mg, 91%) was obtained after Kügelrohr distillation (40−50°/0.09 mmHg): ^{1}H NMR δ 0.83 (6H, d, J = 6.6 Hz), 1.66 (1H, nonet, J = 6.6 Hz), 2.57 (2H, d, J = 6.6 Hz), 6.58 (2H, m), 7.44 (2H, m); ^{13}C NMR δ 20.97, 23.87, 30.12, 106.02 (d, J = 3.5 Hz), 116.60 (d, J = 20.7 Hz), 141.00 (d, J = 7.6 Hz), 163.13 (d, J = 245.7 Hz); ^{125}Te NMR δ 423.73; MS *m*/*z* (relative intensity) 282 (M^+, 14.4), 225 (14), 165 (2), 130 (9), 75 (23), 56 (100); HRMS calcd for $C_{10}H_{13}TeF$ 282.0071, found 282.0072.

Telluroanisole[27] (**36**) was prepared according to the standard protocol (E) using diphenyl ditelluride and iodomethane. Kugelrohr distillation (35−40°/0.08 mmHg) afforded **36** as a red oil (84%): ^{1}H NMR δ 1.77 (3H, s), 6.87−6.99 (3H, m), 7.48−7.55 (2H, m); ^{13}C NMR δ 113.01, 124.70, 127.21, 129.34, 137.01; ^{125}Te NMR δ 337.4.

2-Methyl-1-(phenyltelluro)propane[28] (**37**) was prepared according to the standard protocol (E) using diphenyl ditelluride and 1-bromo-2-methylpropane. Kügelrohr distillation (40−50 °C/0.080 mmHg) afforded **37** as a yellow oil (70%): ^{1}H NMR δ 0.85 (6H, d, J = 6.6 Hz), 1.71 (1H, m), 2.65 (2H, d, J = 6.6 Hz), 6.88−7.03 (3H, m), 7.65−7.68 (2H, m); ^{13}C NMR δ 20.44, 23.95, 30.19, 112.67, 127.47, 129.31, 138.54; ^{125}Te NMR δ 421.2; MS *m*/*z* (relative intensity) 264 (M^+, 8.4), 207 (9), 130 (8), 83 (70), 56 (100); HRMS calcd for $C_{10}H_{14}Te$ 264.0165, found 264.0157.

[(4-Fluorophenyl)telluro]cyclohexane (**40**) was prepared according to the standard protocol (E) using bis(4-fluorophenyl) ditelluride and bromocyclohexane. Kügelrohr distillation (150°/0.6 mmHg) afforded **40** as a yellow oil (99%): ^{1}H NMR δ 1.33 (2H, m), 1.63 (4H, m), 2.07 (4H, q, J = 10.5, 2.7 Hz), 3.43 (1H, m), 6.91 (2H, dd, J = 9, 8.7 Hz), 7.76 (2H, dd, J = 5.7, 8.4 Hz); ^{13}C NMR δ 26.03, 27.25, 28.31, 29.45, 36.49, 105.56, 116.49 (d, J = 20.3 Hz), 143.85 (d, J = 7.6 Hz), 164.49 (d, J = 248.3 Hz); MS *m*/*z* (relative intensity) 308 (M^+, 16.4), 226 (30), 95 (27), 83 (90), 75 (11), 55 (100); HRMS calcd for $C_{12}H_{15}TeF$ 308.0225, found 308.0211.

Standard Protocol (F) for the Preparative-Scale Thermolysis of Alkyl (Aryltelluro)formates. (Phenyltelluro)-

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cyclohexane[29] **(39).** Cyclohexyl (phenyltelluro)formate (**19**, 1.0 g, 3.02 mmol) was dissolved in benzene (1.9 mL, 1.6 M) and heated at 160 °C for 9 d in a sealed glass vessel. Removal of solvent *in vacuo* and flash chromatography (hexane) afforded **39** as a yellow oil (0.62 g, 71%): ^{1}H NMR δ 1.07−2.18 (10H, m), 3.30 (1H, m), 6.92−7.04 (3H, m), 7.80−7.83 (2H, m); ^{13}C NMR δ 26.00, 27.64, 28.25, 36.58, 112.12, 127.92, 129.24, 140.53.

3α- and 3*β*-(Phenyltelluro)cholestane(41)[25] were prepared according to the standard protocol (F) using 3*β*-cholestanyl (phenyltelluro)formate (**22**) in benzene (0.88 M) with heating at 160 °C for 7 d. Removal of solvent *in vacuo* and flash chromatography (hexane) afforded **41** as a mixture of epimers (85%): ^{1}H NMR δ 0.62−2.05 (46H, m), 3.28 (1H, m, *β* isomer), 3.94 (1H, m, α isomer), 7.01 (3H, m), 7.80 (2H, d, J = 6.9 Hz, α isomer), 7.90 (2H, d, J = 6.0 Hz, *β* isomer); ^{125}Te δ 677.8 (α isomer), 591.4 (*β* isomer); MS *m*/*z* (relative intensity) 578 (M$^+$, 5.55), 411 (3), 371 (30), 215 (20), 95 (84), 54 (100). Anal. Calcd for $C_{33}H_{52}Te$: C, 68.77; H, 9.09. Found: C, 68.94; H, 8.92.

1-(Benzylseleno)-5-hexanol. Sodium borohydride (1.1 g, 0.028 mol) was added to a solution of 6-bromo-2-hexanone[30] (5.0 g, 0.028 mol) in dry ethanol (30 mL) under nitrogen and the solution was left to stir for 3 h at room temperature. In a separate reaction vessel, sodium borohydride was added to a solution of dibenzyl diselenide (4.95 g, 0.015 mol) in dry ethanol (200 mL) under nitrogen. After about 3 h, the solution of the reduced ketone was transferred via cannula into the solution containing the sodium benzylselenoate, and the resultant mixture was stirred under nitrogen overnight at room temperature. The solution was poured into saturated $NaHCO_3$ (50 mL), extracted with ether, and dried ($MgSO_4$), and the solvent was removed *in vacuo*. The residue was subjected to flash chromatography (hexane/ethyl acetate 7:3), and the title compound was isolated as a yellow oil (5.14 g, 68%): ^{1}H NMR ($CDCl_3$) δ 1.17 (3H, d, J = 6.0 Hz), 1.38−1.65 (7H, m), 2.49 (2H, t, J = 7.2 Hz), 3.73−3.83 (1H, m), 3.77 (2H, s), 7.18−7.34 (5H, m); ^{13}C NMR ($CDCl_3$) δ 23.44, 23.88, 25.98, 26.94, 30.12, 38.62, 67.85, 126.55, 128.40, 128.75, 139.49; ^{77}Se NMR ($CDCl_3$) δ 256.13; IR ν (OH stretch) 3368 cm^{-1}. MS *m*/*z* (relative intensity) 272 (M$^+$, 3.7), 108 (90), 99 (15), 79 (100), 59 (74), 45 (74). Anal. Calcd for $C_{13}H_{20}OSe$: C, 57.56; H, 7.43. Found: C, 57.63; H, 7.50.

1-(Benzylseleno)-5-hexyl (Phenylthiono)formate (4). Phenyl chlorothionoformate (477 mg, 2.77 mmol) and pyridine (4.7 g, 60 mmol) were added to a solution of 1-(benzylseleno)-5-hexanol (500 mg, 1.84 mmol) in dichloromethane (10 mL). The solution was shielded from light while being stirred under nitrogen overnight at room temperature. The resulting yellow solution was poured into water (30 mL) and extracted with ethyl acetate (2 × 25 mL). The combined organic extracts were washed with 10% HCl (20 mL) and then saturated $NaHCO_3$ (20 mL) and dried ($MgSO_4$). Removal of the solvent *in vacuo* gave an orange oil which, upon purification by flash chromatography (hexane/ethyl acetate 99:1), gave the title compound as a low-melting, white solid (598 mg, 80%): ^{1}H NMR δ 1.16 (3H, d, J = 6.3 Hz), 1.17−1.61 (6H, m), 2.22 (2H, t, J = 7.2 Hz), 3.52 (2H, s), 5.38 (1H, m), 6.88−7.19 (10H, m); ^{13}C NMR δ 19.01, 23.58, 25.63, 27.01, 30.15, 35.03, 81.95, 122.14, 122.44, 126.37, 126.67, 126.78, 128.62, 129.20, 129.62, 129.75, 140.04, 154.00, 154.15, 195.09; ^{77}Se NMR ($CDCl_3$) δ 258.04; MS *m*/*z* (relative intensity) 260 (2.2), 258 (12), 214 (29), 141 (14), 94 (27), 91 (100). Anal. Calcd for $C_{20}H_{24}O_2SSe$: C, 58.96; H, 5.94. Found: C, 58.77; H, 6.05.

1-[(Tributylstannyl)seleno]-5-hexyl (Phenylthiono)formate (5). Tri-*n*-butyltin hydride (230 mg, 0.80 mmol) was added to a solution of 1-(benzylseleno)-5-hexyl (phenylthiono)formate (**4**, 214 mg, 0.53 mmol) in benzene (20 mL, 0.03 M). AIBN was added, and the solution was heated under nitrogen at reflux overnight. The solvent was removed *in vacuo*, and the resulting yellow oil was purified by preparative TLC (hexane/ethyl acetate 98:2) to give the title compound as an unstable pale oil with a distinctive pungent odor (94.1 mg, 30%): ^{1}H NMR ($CDCl_3$) δ 0.91 (9H, t, J = 7.2 Hz), 1.14−1.86 (27H, m), 2.56 (2H, t, J = 7.2 Hz), 5.38 (1H, m), 7.11 (2H, d, J = 8.1 Hz), 7.28 (1H, app t, J = 6.6 Hz), 7.41 (2H, app t, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 13.23, 13.63, 16.74, 19.03, 25.42, 27.02, 28.98, 34.20, 34.88, 82.16, 122.02, 126.36, 129.38, 153.30, 194.47; ^{77}Se NMR ($CDCl_3$) δ −209.78; ^{119}Sn NMR ($CDCl_3$) δ 51.29; MS *m*/*z* (relative intensity) 551 (0.4), 315 (2), 271 (10), 269 (26), 265 (11), 94 (100).

1-(Benzylseleno)-5-hexyl (phenyltelluro)formate (**44**) was prepared according to the standard protocol (B) using 1-(benzylseleno)-5-hexanol and diphenyl ditelluride. Flash chromatography (hexane/ethyl acetate 98:2) afforded the telluroformate **44** as a yellow oil (68%): ^{1}H NMR δ 0.81−1.35 (6H, m), 0.97 (3H, d, J = 6.0 Hz), 2.17 (2H, t, J = 7.5 Hz), 3.51 (2H, s), 4.99 (1H, m), 6.96−7.18 (8H, m), 7.79−7.83 (2H, m); ^{13}C NMR δ 20.20, 23.49, 25.77, 26.94, 30.07, 35.54, 75.49, 114.21, 126.77, 128.61, 129.21, 129.54, 139.97, 140.05, 156.20; ^{77}Se NMR δ 259.5; ^{125}Te NMR δ 770.2; IR ν (C=O) 1708 cm^{-1}; MS *m*/*z* (relative intensity) 300 (3.7), 163 (6), 135 (1), 91 (100), 83 (3). Anal. Calcd for $C_{20}H_{24}O_2SeTe$: C, 47.76; H, 4.81. Found: C, 48.07; H, 5.17.

1,1-Dibromo-2-methylselenane[26] (**46**) was prepared according to the standard protocol (F) using 1-(benzylseleno)-5-hexyl (phenyltelluro)formate (**44**, 696 mg, 1.38 mmol) and benzene (2 mL) with heating at 160 °C for 14 d. Benzene (20 mL) was added, and the solution was distilled at atmospheric pressure (2-methylselenane azotropes with benzene). A dilute solution of bromine in CCl_4 was added dropwise to the distillate until the bromine color persisted. The benzene was removed *in vacuo* to give the title compound **46** as a yellow/red gum (332 mg, 74%): ^{1}H NMR δ ($CDCl_3$) 1.58−2.54 (6H, m), 1.62 (3H, d, J = 6.6 Hz), 3.85−3.89 (1H, m), 4.16 (1H, td, J = 4.5, 4.2, 4.5 Hz), 4.41 (1H, m); ^{13}C NMR ($CDCl_3$) δ 19.16, 20.24, 24.26, 29.52, 50.87, 63.88; ^{77}Se NMR ($CDCl_3$) δ 568.7.

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