Palladium-Mediated Reactions of Chloroformates with Phenylselenotris(trimethylsilyl)silane and Aryltellurotris(trimethylsilyl)silane: Improved Procedure for the Preparation of (Phenylseleno)- and (Aryltelluro)formates

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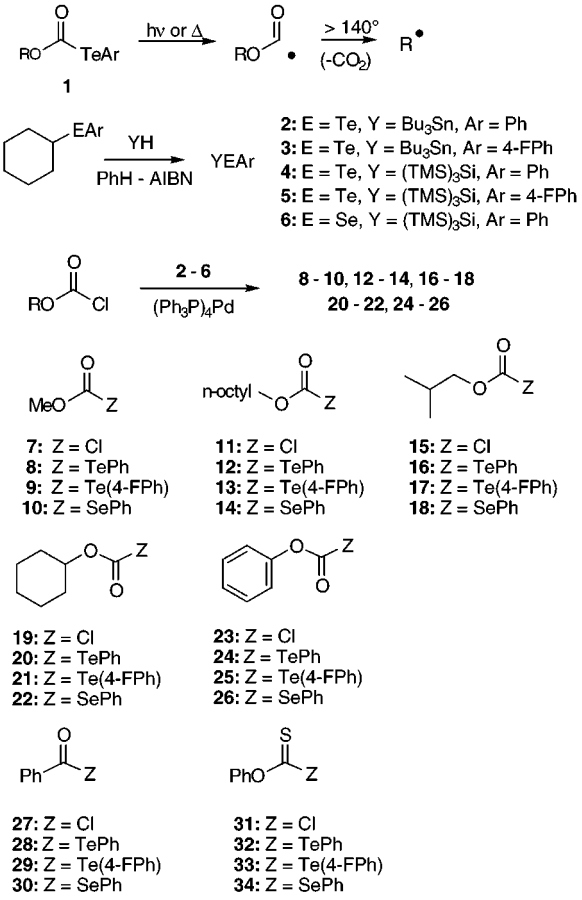
Recently, we reported that (aryltelluro)formates (**1**) are effective precursors of both alkyl and oxyacyl radicals.[1] Oxyacyl radicals are generated by either thermolysis or photolysis of **1**, which at temperatures of 140−160° C decarboxylate to afford the corresponding alkyl radical.



Despite the potential of telluroformates in free-radical synthesis, current methods for their preparations are somewhat limited. Our procedure for the preparation of **1** involves the reaction of a chloroformate with sodium aryltelluroate, itself prepared by the sodium borohydride reduction of the corresponding diaryldittelluride in THF. While the required telluroformates were obtained in excellent yields, problems associated with adventitious oxygen and some classes of unsaturated substrate are major drawbacks.[2] Consequently, we were unable to prepare the (aryltelluro)formates (**24** and **25**) derived from phenyl chloroformate.

Transition metal-catalyzed cross-coupling reactions are of enormous synthetic value.[3] With this in mind and with the aim of providing an improved procedure for the preparation of (aryltelluro)formates, we began to explore the reactions of several chloroformates (**7**, **11**, **15**, **19**, and **23**) with phenyltellurotributylstannane (**2**) as well as with phenyltellurotris(trimethylsilyl)silane (**4**) and (4-fluorophenyl)tellurotris(trimethylsilyl)silane (**5**) in the presence of tetrakis(triphenylphosphine)palladium [$(Ph_3P)_4Pd$] to afford the corresponding telluroformate (**8**, **9**, **12**, **13**, **16**, **17**, **20**, **21**, **24**, and **25**) in 68−83% yield. This chemistry is also amenable to the preparation of (phenylseleno)formates (**10**, **14**, **18**, **22**, and **26**) and (phenylseleno)- and (phenyltelluro)esters (**28**−**30**), as well as (phenylseleno)- and (phenyltelluro)thionoformates (**32**−**34**). For example, when **4** is replaced with the selenium analogue, phenylselenotris(trimethylsilyl)silane (**6**), the selenoformate is obtained in 79−87% yield.

Results and Discussion

During recent studies into the reversibility of radical reactions involving aryltellurides, we had cause to prepare phenyltellurotributyltin (**2**) and (4-fluorophenyl)-tellurotributyltin (**3**).[4] These coupounds are not isolable, but are prepared in situ by the reaction of the aryltellurocyclohexane with tributyltin hydride (AIBN initiator) and can be characterized by ^{119}Sn and ^{125}Te NMR spectroscopy.[4] When methyl chloroformate (**7**) (1.0 equiv) was introduced into a benzene solution of **2** (70 mg) in a NMR tube and the reaction mixture allowed to stand at room temperature overnight, or heated at 80 °C for 4 h, no reaction was observed by ^{1}H, ^{119}Sn, and ^{125}Te NMR spectroscopy. When tetrakis(triphenylphosphine)palladium (4 mol %)[5] was added to the solution and the resultant dark red mixture allowed to stand at room temperature for 2 h, ^{119}Sn and ^{125}Te NMR spectroscopy revealed the absence of **2** (^{125}Te δ −209.4; ^{119}Sn δ −1.3) and the presence of methyl (phenyltelluro)formate[1] (**8**) (^{125}Te δ 771.4) and minor quantities of diphenyl ditelluride (^{125}Te δ 420). Unfortunately, due to the poor chromatographic properties of organostannanes,[6] **8** proved to be difficult to separate from the tin byproducts; careful flash chromatography afforded **8** in 60% yield as a yellow oil contaminated with small amounts of tin byproducts.

Given the superior chromatographic properties of organosilanes compared to those of their tin counterparts and given the ready availability of tris(trimethylsilyl)-silane for use in radical chemistry,[7] we began to explore

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(5) Calalyst quantities of 3−5 mol % were used; varations within this range lead to increases or decreases in reaction time of up to 4 h from the times quoted in Table 1.

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the analogous silane chemistry. Phenyltellurotris(trimethylsilyl)silane (**4**) and (4-fluorophenyl)tellurotris(trimethylsilyl)silane (**5**) were prepared in a fashion analogous to that of their tin counterparts. Accordingly, tris(trimethylsilyl)silane (1.0 equiv) was reacted (in the dark) for 2 h with the required aryltellurocyclohexane[1] (0.4 M) in benzene (80 °C, AIBN initiator).

As was observed for stannanes (**2** and **3**), the tellurosilanes (**4** and **5**) proved to be light sensitive and generally unstable, and attempted removal of the solvent resulted in rapid decomposition. In benzene, under nitrogen, and in the dark, they appear to have an indefinite lifetime.

The tellurosilanes (**4** and **5**) can be characterized by ^{1}H, ^{13}C, ^{29}Si, and ^{125}Te NMR spectroscopy. Specifically, **4** exhibits a singlet at δ −192.9 in the ^{125}Te NMR spectrum and two singlets at δ −10.6 and −93.3 in the ^{29}Si NMR spectrum, while **5** exhibits singlets at δ −195.9 (^{125}Te) and −10.5 and −92.6 (^{29}Si).

When the previously prepared solution of **4** was reacted with methyl chloroformate (**7**) (1.0 equiv) and tetrakis(triphenylphosphine)palladium (4 mol %)[5] and the dark red mixture allowed to stand for 6 h, ^{125}Te NMR spectroscopy revealed the absence of **4** and the presence of methyl (phenyltelluro)formate (**8**) and small amounts of diphenyl ditelluride, while ^{29}Si NMR spectroscopy revealed two signals which we have assigned to chlorotris(trimethylsilyl)silane (δ 1.9 and −11.3) by comparison with other chlorosilanes.[8] Simple flash chromatography afforded **8** in 80% yield which was free from contamination. Similarly, reaction of **5** with **7** and $(Ph_3P)_4Pd$ afforded methyl [(4-fluorophenyl)telluro]formate[1] (**9**) which was isolated in 71% yield as a yellow oil after flash chrotmatography.

To our delight, application of this methodology to a representative set of primary, secondary, and aromatic chloroformates afforded the corresponding telluroformates in 68−83% yield (Table 1). Importantly, phenyl (phenyltelluro)formate (**28**) and phenyl [(4-fluorophenyl)telluro]formate (**29**) were able to be isolated in 79 and 81% yield respectively following this procedure. All reactions were carried out at either 25, (RT) or 80 °C with reaction times, as determined by ^{125}Te NMR spectroscopy, varying from 6 to 12 h depending on the alkyl substituent and catalyst concentration; 4 mol % $(Ph_3P)_4Pd$[5] and reaction concentrations between about 0.4 and 0.7 M proved to be optimal for our requirements. Lower reaction concentrations invariably resulted in the precipitation of a fine black powder, presumably, elemental tellurium, while the formation of diaryldittelluride could be observed at higher concentrations.

When phenyltellurotris(trimethylsilyl)silane (**4**) was replaced with phenylselenotris(trimethylsilyl)silane (**6**), itself prepared by the reaction of phenylselenocyclohexane[1] with tris(trimethylsilyl)silane under standard contitions, methyl, primary, secondary, and (phenylseleno)formates (**10**, **14**, **18**, **22**, and **26**) could be isolated in 79−87% yield. These reactions appear to be slower than their tellurium counterparts; most reactions were complete in 18 h.

This protocol was also successfully applied to the preparation of telluro- and selenoesters. ^{125}Te NMR spectroscopy revealed that benzoyl chloride (**27**) reacts with **4** and **5** to give products consistent with phenyltelluro benzoate (**28**) (^{125}Te δ 942) and (4-fluorophenyl)telluro benzoate (**29**, R = Ph) (^{125}Te δ 930).[9] These telluroesters proved to be substantially more light sensitive than the corresponding telluroformates. While background light proved not to be problematic during chromatographic purification of the telluroformates, acceptable yields of **28** and **29** could only be obtained by chromatography performed in a darkened environment with the column wrapped in aluminum foil. Under these conditions, **28** and **29** were isolated in 87% yield. When benzoyl chloride was reacted with phenylselenotris(trimethylsilyl)silane (**6**) and $(Ph_3P)_4Pd$ under the previously described reaction conditions, phenylseleno benzoate (**30**) was isolated in 81% yield after flash chromatography.

Finally, to assess the applicability of this procedure to the preparation of (aryltelluro)- and (phenylseleno)thionoformates, commercially available phenyl chlorothionoformate (**31**) was reacted with **4**−**6** under the described conditions. To our delight, the corresponding thionoformates (**32**−**34**) were isolated in 86−96% yield after chromatography. These reactions proved to be substantially faster than those involving the previously described chloroformates, requiring only 5 min at 25 °C for the preparation of **32** and **33** and 40 min at 25 °C for **34**.

In conclusion, we have demonstrated that phenyltellurotris(trimethylsilyl)silane (**4**) and (4-fluorophenyl)tellurotris(trimethylsilyl)silane (**5**) are effective reagents for the palladium-catalyzed preparation of (phenyltelluro)formates and [(4-fluorophenyl)telluro]formates, respectively. These reagents have an advantage over their tin counterparts (**2** and **3**) in that simple flash chromatography affords pure compounds in good yield. This

Table 1. Reactions of Some Chloroformates, Benzoyl Chloride, and Phenyl Chlorothionoformate with Phenyltellurotributyltin (2) and Arylchalcogenotris(trimethylsilyl)silanes (4−6) in the Presence of 4 mol % Tetrakis(triphenylphosphine)palladium

substrate	reagent	product	reaction time (temperature) (°C)	yield (%)	NMR	ref
7	**2**	**8**	2 h (25)	60[a]	771 (^{125}Te)	1
7	**4**	**8**	6 h (25)	80		
7	**5**	**9**	9 h (25)	71	765 (^{125}Te)	1
7	**6**	**10**	15 h (25)	87	506 (^{77}Se)	1
11	**4**	**12**	6 h (80)	83	770 (^{125}Te)	*b*
11	**5**	**13**	9 h (80)	75	771 (^{125}Te)	*b*
11	**6**	**14**	18 h (80)	79	505 (^{77}Se)	*b*
15	**4**	**16**	8 h (80)	68	769 (^{125}Te)	1
15	**5**	**17**	8 h (80)	77	760 (^{125}Te)	1
15	**6**	**18**	18 h (80)	83	506 (^{77}Se)	1
19	**4**	**20**	8 h (80)	72	771 (^{125}Te)	1
19	**5**	**21**	8 h (80)	72	770 (^{125}Te)	1
19	**6**	**22**	18 h (80)	83	509 (^{77}Se)	1
23	**4**	**24**	10 h (80)	79	794 (^{125}Te)	*b*
23	**5**	**25**	12 h (80)	81	789 (^{125}Te)	*b*
23	**6**	**26**	18 h (80)	86	515 (^{77}Se)	*b*
27	**4**	**28**	6 h (80)	87	942 (^{125}Te)	*b*
27	**5**	**29**	8 h (80)	87	930 (^{125}Te)	9
27	**6**	**30**	18 h (80)	81	636 (^{77}Se)	10
31	**4**	**32**	5 min (25)	86	1164 (^{125}Te)	*b*
31	**5**	**33**	5 min (25)	91	1156 (^{125}Te)	*b*
31	**6**	**34**	40 min (25)	96	738 (^{77}Se)	*b*

[a] Contaminated with stannane residues (see the text). [b] This work.

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protocol is also amenable to the preparation of (phenylseleno)- and (aryltelluro)esters as well as (phenylseleno)- and (aryltelluro)thionoformates in excellent yields.

Experimental Section

Methyl chloroformate, *iso*-butyl chloroformate, phenyl chloroformate, benzoyl chloride, phenyl chlorothionoformate, tetrakis(triphenylphosphine)palladium, and tris(trimethylsilyl)-silane were purchased from Aldrich. Octyl chloroformate and cyclohexyl chloroformate were prepared by reaction of the corresponding alcohol with phosgene.[1] (Phenyltelluro)cyclohexane, [(4-fluorophenyl)telluro]cyclohexane, and (phenylseleno)-cyclohexane were prepared according to our previously published procedure.[4] All melting points are uncorrected. Elemental analyses were carried out by Chemical and Micro Analytical Services Pty. Ltd.

Standard Protocol A for the Preparation of (Arylchalcogeno)formates, Benzoates, and Thionoformates. Methyl (Phenyltelluro)formate (8).[1] Tris(trimethylsilyl)silane (110 μL, 89 mg, 360 μmol) and AIBN (ca. 1 crystal) were added to a solution of (phenyltelluro)cyclohexane (103 mg, 360 μmol) in benzene (900 μL). The reaction vessel was sealed (septum), purged with nitrogen, and heated at 80 °C, for 2 h while it was shielded from background light. After the mixture cooled to RT, tetrakis(triphenylphosphine)palladium (21 mg, 18 μmol) and methyl chloroformate (28 mg, 23 μL, 358 μmol) were added, and the mixture was briefly shaken vigorously and allowed to stand at RT (25 °C), while it was shielded from light, for 6 h, at which time TLC analysis revealed the presence of a dominant product. The solvent was removed in vacuo and the residue separated by flash chromatography (30:1 petroleum ether/ethyl acetate) to afford **8** as a yellow oil which exhibited properties identical to those reported previously (61 mg, 80%).

Methyl [(4-fluorophenyl)telluro]formate (9), methyl (phenylseleno)formate (10), octyl (phenyltelluro)formate (12), octyl (phenylseleno)formate (14), 2-methyl-1-propyl (phenyltelluro)formate (16), 2-methyl-1-propyl [(4-fluorophenyl)telluro]formate (17), 2-methyl-1-propyl (phenylseleno)formate (18), cyclohexyl (phenyltelluro)formate (20), cyclohexyl [(4-fluorophenyl)telluro]formate (21), cyclohexyl (phenylseleno)formate (22), (4-fluorophenyl)-telluro benzoate (29), and phenylseleno benzoate (30) were prepared according to standard protocol A using benzoyl chloride or the appropriate alkyl chloroformate together with the (arylchalcogeno)cyclohexane for the reaction times listed (Table 1) and isolated in the yields indicated in Table 1. These compounds exhibited physical properties identical to those reported previously.[1,9,10]

Octyl [(4-fluorophenyl)telluro]formate (13), phenyl (phenyltelluro)formate (24), phenyl [(4-fluorophenyl)telluro]formate (25), phenyl (phenylseleno)formate (26), phenyltelluro benzoate (28), phenyl (phenyltelluro)-thionoformate (32), phenyl [(4-fluorophenyl)telluro]thionoformate (33), and phenyl (phenylseleno)thionoformate (34) were prepared according to standard protocol A using benzoyl chloride, phenyl chlorothionoformate, or the appropriate alkyl chloroformate, together with the (arylchalcogeno)cyclohexane, for the reaction times listed (Table 1) and isolated in the yields indicated in Table 1.

Octyl [(4-fluorophenyl)telluro]formate (13) (oil): ^{1}H NMR ($CDCl_3$) δ 0.86−0.90 (3H, m), 1.23−1.32 (10H, m), 1.61−1.68 (2H, m), 4.28 (2H, t, J = 7.5 Hz), 6.99 (2H, m), 7.80 (2H, m); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 25.8, 28.7, 29.1, 29.7, 31.7, 68.3, 107.6, 116.9 [($J(^{13}C-^{19}F)$ = 21.1 Hz], 142.1 [$J(^{13}C-^{19}F)$ = 7.6 Hz], 163.5 [$J(^{13}C-^{19}F)$ = 249.7 Hz]; ^{125}Te NMR (C_6D_6) δ 771; IR ν (C=O) (KBr) 1776 cm^{-1}; MS m/z (relative intensity) 382 (M^+, 25), 339 (16), 225 (46), 59 (100); HRMS $C_{15}H_{21}FO_2{}^{130}Te$ calcd 382.0588, found 382.0571.

Phenyl (phenyltelluro)formate (24): mp 75−76 °C; ^{1}H NMR ($CDCl_3$) δ 7.18−7.41 (8H, m), 7.87 (2H, d, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 113.7, 121.9, 126.6, 129.4, 129.5, 129.6, 139.8, 151.4, 156.9; ^{125}Te NMR (C_6D_6) δ 794; IR ν (C=O) (KBr) 1730 cm^{-1}; MS m/z (relative intensity) 328 (M^+, 8), 300 (25), 207 (100). Anal. Calcd for $C_{13}H_{10}O_2Te$: C, 47.9; H, 3.4. Found: C, 48.0; H, 3.1.

Phenyl [(4-fluorophenyl)telluro]formate (25): mp 76−77 °C; ^{1}H NMR ($CDCl_3$) δ 7.00 (2H, t, J = 7.5 Hz), 7.15−7.38 (5H, m), 7.78−7.83 (2H, m); ^{13}C NMR ($CDCl_3$) δ 107.8, 117.1 [$J(^{13}C-^{19}F)$ = 21.2 Hz], 121.8, 126.6, 129.5, 142.1 [$J(^{13}C-^{19}F)$ = 8.0 Hz], 151.3, 163.5 [$J(^{13}C-^{19}F)$ = 250.2 Hz]; ^{125}Te NMR (C_6D_6) δ 789; IR ν (C=O) (KBr) 1776 cm^{-1}; MS m/z (relative intensity) 346 (M^+, 20), 318 (62), 223 (100); HRMS $C_{13}H_9FO_2{}^{130}Te$ calcd 345.9649, found 345.9650.

Phenyl (phenylseleno)formate (26): mp 60−63 °C; ^{1}H NMR (C_6D_6) δ 6.48−6.71 (7H, m), 6.86 (1H, s), 7.22−7.28 (2H, m); ^{13}C NMR (C_6D_6) δ 113.6, 126.9, 128.9, 129.0, 129.5, 133.9, 140.3, 142.7; ^{77}Se NMR (C_6D_6) δ 515; IR ν (C=O) (KBr) 1730 cm^{-1}; MS m/z (relative intensity) 278 (M^+, 10), 250 (80), 157 (100). Anal. Calcd for $C_{13}H_{10}O_2Se$: C, 56.3; H, 3.6. Found: C, 56.3; H, 3.4.

Phenyltelluro benzoate (28): mp 66−68.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.32−7.47 (5H, m), 7.59 (1H, t, J = 7.5 Hz), 7.72−7.80 (4H, m); ^{13}C NMR ($CDCl_3$) δ 113.7, 121.9, 126.6, 129.4, 129.5, 129.6, 139.8, 151.4, 156.9; ^{125}Te NMR (C_6D_6) δ 941; IR ν (C=O) (KBr) 1669 cm^{-1}. Anal. Calcd for $C_{13}H_{10}OTe$: C, 50.4; H, 3.3. Found: C, 50.2; H, 3.5.

Phenyl (phenyltelluro)thionoformate (32): mp 44.5−46 °C; ^{1}H NMR ($CDCl_3$) δ 7.15 (2H, d, J = 7.6 Hz), 7.25−7.46 (6H, m), 7.94 (2H, m); ^{13}C NMR ($CDCl_3$) δ 119.3, 122.0, 126.7, 129.5, 129.6, 129.8, 140.3, 155.3, 207.2; ^{125}Te NMR (C_6D_6) δ 1164; MS m/z (relative intensity) 344 (M^+, 48), 207 (57), 137 (100); HRMS $C_{13}H_{10}O^{35}S^{130}Te$ calcd 343.9515, found 343.9494.

Phenyl [(4-fluorophenyl)telluro]thionoformate (33): mp 84.5−85 °C; ^{1}H NMR ($CDCl_3$) δ 7.04−7.12 (3H, m), 7.29 (2H, m), 7.41 (2H, t, J = 7.8 Hz), 7.87−7.92 (2H, m); ^{13}C NMR ($CDCl_3$) δ 113.7, 117.3 [$J(^{13}C-^{19}F)$ = 21.4 Hz], 122.0, 126.7, 129.6, 142.7 [$J(^{13}C-^{19}F)$ = 7.5 Hz], 155.2, 163.6 [$J(^{13}C-^{19}F)$ = 250.2 Hz), 207.1; ^{125}Te NMR (C_6D_6) δ 1156; MS m/z (relative intensity) 362 (M^+, 100), 225 (83), 139 (90). Anal. Calcd for $C_{13}H_9FOSTe$: C, 43.4; H, 2.5. Found: C, 43.1; H, 2.5.

Phenyl (phenylseleno)thionoformate (34): mp 47−48 °C; ^{1}H NMR ($CDCl_3$) δ 7.07 (2H, d, J = 8.1 Hz), 7.20−7.43 (6H, m), 7.70 (2H, m); ^{13}C NMR ($CDCl_3$) δ 121.8, 126.6, 129.4, 129.5, 129.7, 136.1, 154.9, 213.2; ^{77}Se NMR (C_6D_6) δ 738; MS m/z (relative intensity) 294 (M^+, 57), 264 (78), 154 (100). Anal. Calcd for $C_{13}H_{10}OSSe$: C, 53.2; H, 3.4. Found: C, 53.6; H, 3.1.

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