PERKIN 1 COMMUNICATION

Phenylselenotris(trimethylsilyl)silane and phenyltellurotris(trimethylsilyl)silane: versatile reagents for the preparation of phenylseleno- and phenyltelluro-formates

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Phenyltellurotris(trimethylsilyl)silane 4 and (4-fluorophenyltelluro)tris(trimethylsilyl)silane 5 react with methyl, 2-methylpropyl, cyclohexyl and phenyl substituted chloroformates (7, 11, 15, 19) in benzene and in the presence of tetrakis(triphenylphosphine)palladium(0) (4 mol%) to afford the corresponding aryltelluroformate (8, 9, 12, 13, 16, 17, 20, 21) in 50–79% yield; this procedure is also applicable to the preparation of (phenylseleno)formates and seleno- and telluro-esters.

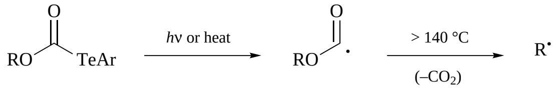
Recently, we reported that (aryltelluro)formates **1** are effective precursors of both alkyl and oxyacyl radicals.[1] Our procedure for the preparation of **1** involves the reaction of a chloroformate with sodium aryl telluride, itself prepared by the sodium borohydride reduction of the corresponding diaryl ditelluride in THF. While the required telluroformates were obtained in excellent yields, problems associated with adventitious oxygen and some classes of aromatic substrate† are major drawbacks.[2]

Recognising that transition metal catalyzed cross-coupling reactions are of enormous synthetic value[3] and with the aim of providing an improved procedure for the preparation of (aryltelluro)formates, we began to explore the reactions of several chloroformates with phenyltellurotributyltin **2** as well as phenyltellurotris(trimethylsilyl)silane **4** and (4-fluorophenyltelluro)tris(trimethylsilyl)silane **5** in the presence of tetrakis(triphenylphospine)palladium(0) [$(Ph_3P)_4Pd$].

During recent studies into the reversibility of radical reactions involving aryl tellurides, we had cause to prepare phenyltellurotributyltin **2** and (4-fluorophenyltelluro)tributyltin **3**.[4] These compounds are not isolable, but are prepared *in situ* by the reaction of the (aryltelluro)cyclohexane with tributyltin hydride (AIBN initiator) and can be characterised by ^{119}Sn and ^{125}Te NMR spectroscopy.[4,5] When methyl chloroformate **7** (1.0 equiv.) was introduced into a benzene solution of **2** (70 mg) in an NMR tube and the reaction mixture allowed to stand at room temperature overnight, or heated at 80 °C for four hours, no reaction was observed by ^{1}H, ^{119}Sn and ^{125}Te NMR spectroscopy. When tetrakis(triphenylphosphine)palladium(0) (4 mol%) 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 poor chromatographic properties of organostannanes,[6] **8** proved difficult to separate from the tin by-products; careful flash chromatography afforded **8** in 60% yield as a yellow oil contaminated with small amounts of tin by-products.

Given the superior chromatographic properties of organosilanes over their tin counterparts and given the ready availability of tris(trimethylsilyl)silane for use in radical chemistry,[7] we began to explore the analogous silane chemistry. Phenyltellurotris(trimethylsilyl)silane **4** and (4-fluorophenyltelluro)tris(trimethylsilyl)silane **5** were prepared in an analogous fashion to their tin counterparts. Accordingly, tris(trimethylsilyl)silane (1.0 equiv.) was reacted (in the dark) for 2 h with the required (aryltelluro)cyclohexane[1] (0.7 M) in benzene (80 °C, AIBN initiator).‡ As was observed for stannanes (**2**, **3**), the tellurosilanes (**4**, **5**) proved to be light sensitive and generally unstable, 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**, **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), δ −10.5 and −92.6 (^{29}Si).



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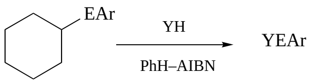
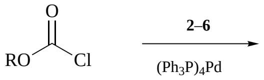
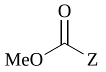


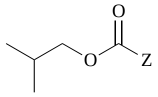
2 E = Te, Y = Bu_3Sn, Ar = Ph
3 E = Te, Y = Bu_3Sn, Ar = 4-FPh
4 E = Te, Y = $(TMS)_3Si$, Ar = Ph
5 E = Te, Y = $(TMS)_3Si$, Ar = 4-FPh
6 E = Se, Y = $(TMS)_3Si$, Ar = Ph



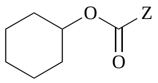
8–10, 12–14, 16–18, 20–22



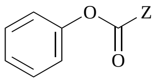
7 Z = Cl
8 Z = TePh
9 Z = Te(4-FPh)
10 Z = SePh



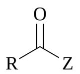
11 Z = Cl
12 Z = TePh
13 Z = Te(4-FPh)
14 Z = SePh



15 Z = Cl
16 Z = TePh
17 Z = Te(4-FPh)
18 Z = SePh



19 Z = Cl
20 Z = TePh
21 Z = Te(4-FPh)
22 Z = SePh



23 Z = Cl
24 Z = TePh
25 Z = Te(4-FPh)
26 Z = SePh

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† In our hands, addition of a THF solution of phenyl chloroformate to a colourless solution of sodium phenyl telluride in the usual way (see ref. 1) resulted in rapid formation of the (characteristic) red diphenyl ditelluride solution. Consequently, we were unable to prepare the (aryltelluro)formates (**20**, **21**) derived from phenyl chloroformate. The details of the chemistry involved are unclear.

‡ The quality of the glassware is crucial to the success of this reaction. The results quoted in Table 1 were obtained when reactions were carried out in high-quality borosilicate NMR tubes. We were unable to prepare **4** or **5** in 'ordinary' Pyrex glassware and are currently examining this result further.

Table 1 Reactions of some chloroformates and acid chlorides with phenyltellurotributyltin **2** and arylchalcogenotris(trimethylsilyl)silanes (**4**, **5**, **6**) in the presence of catalytic tetrakis(triphenylphosphine)palladium(0)

Substrate	Reagent	Product	*t*/h (*T*/°C)	Yield (%)	*δ*(ppm)	Ref.
7	**2**	**8**	2 (25)	60[a]	771.4 (^{125}Te)	1
7	**4**	**8**	2 (25)	79		
7	**5**	**9**	2 (25)	71	765.3 (^{125}Te)	1
7	**6**	**10**	16 (25)	87	506.3 (^{77}Se)	1
11	**4**	**12**	8 (25)	61	768.9 (^{125}Te)	1
11	**5**	**13**	8 (25)	77	760.3 (^{125}Te)	1
11	**6**	**14**	7 (40)	83	505.2 (^{77}Se)	1
15	**4**	**16**	16 (25)	72	771.6 (^{125}Te)	1
15	**5**	**17**	16 (25)	72	769.9 (^{125}Te)	1
15	**6**	**18**	16 (40)	83	509.3 (^{77}Se)	1
19	**4**	**20**	16 (25)	64	793.7 (^{125}Te)	*b*
19	**5**	**21**	16 (25)	51	789.9 (^{125}Te)	*b*
19	**6**	**22**	16 (40)	72	514.7 (^{77}Se)	*b*
23 (R = Me)	**4**	**24** (R = Me)	2 (25)	59	975.7 (^{125}Te)	*b*
23 (R = Ph)	**5**	**25** (R = Ph)	16 (25)	87	930.3 (^{125}Te)	9
23 (R = Ph)	**6**	**26** (R = Ph)	16 (25)	81	634.6 (^{77}Se)	10

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

When the previously-prepared solution of **4** was reacted with methyl chloroformate **7** (1.0 equiv.) and tetrakis(triphenylphosphine)palladium(0) (4 mol%) and the dark red mixture allowed to stand for 2 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, −11.3) by comparison with other chlorosilanes.[8] Simple flash chromatography afforded **8** in 79% yield and 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 chromatography.

To our delight, application of this methodology to a representative set of primary, secondary and aromatic chloroformates afforded the corresponding telluroformates in 51–79% yield (Table 1). Importantly, phenyl (phenyltelluro)formate **20** and phenyl [(4-fluorophenyl)telluro]formate **21** were able to be isolated in 64 and 51% yield respectively following this procedure.§ All reactions were carried out at 25 °C (room temperature) with reaction times, as determined by ^{125}Te NMR spectoscopy, varying from 2 to 16 h depending on the alkyl substituent.

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 conditions, methyl, primary, secondary and phenyl selenoformates (**10**, **14**, **18**, **22**, **25**) could be isolated in 72–87% yield. These reactions appear to be slower than their tellurium counterparts; elevated temperatures (40 °C) were required for complete conversion of most substrates in a 16 h time frame.

This protocol was also successfully applied to the preparation of telluro- and seleno-esters. ^{125}Te NMR Spectroscopy revealed that acetyl chloride (**23**: R = Me) and benzoyl chloride (**23**: R = Ph) react with **4** and **5** to give products consistent with *Te*-phenyl telluroacetate (**24**: R = Me) (^{125}Te, δ 975.7) and *Te*-(4-fluorophenyl) tellurobenzoate (**25**: R = Ph) (^{125}Te, δ 930.3).[10] 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 **24** and **25** could only be obtained by chromatography performed in a darkened environment with the column wrapped in aluminium foil. Under these conditions, **24** (R = Me) and **25** (R = Ph) were isolated in 59 and 87% respectively. When benzoyl chloride was reacted with phenylselenotris(trimethylsilyl)silane **6** and $(Ph_3P)_4Pd$ under the previously described reaction conditions, *Se*-phenyl selenobenzoate (**25**: R = Ph) was isolated in 81% yield after flash chromatography.

In conclusion, we have demonstrated that phenyltellurotris(trimethylsilyl)silane **4** and (4-fluorophenyltelluro)tris(trimethylsilyl)silane **5** are effective reagents for the palladium-catalyzed preparation of (phenyltelluro)formates and [(4-fluorophenyl)telluro]formates respectively. These reagents have the advantage over their tin counterparts (**2**, **3**) in that simple flash chromatography affords pure compounds in good yield. This protocol is also amenable to the preparation of seleno- and telluro-esters (**24**–**26**) which were obtained from the corresponding acid chloride in good yields.

We are further examining the synthetic utility of these chalcogenosilanes.

Acknowledgements

We thank the Australian Research Council for financial support and an Australian Postgraduate Award to M. A. S.

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Paper 7/04402J
Received 23rd *June* 1997
Accepted 10th *July* 1997

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§ All new compounds gave satisfactory NMR and mass spectral data.