Reversibility in free-radical reactions of aryltellurides with tributylstannyl radical

Carl H. Schiesser* and Melissa A. Skidmore

School of Chemistry, The University of Melbourne, Parkville, Victoria, Australia, 3052

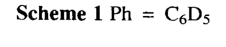
^{119}Sn and ^{125}Te NMR spectroscopies reveal that methyl, primary and secondary alkyl radicals, generated by reaction of phenyltelluroalkanes 4, 6, 7 with tributyltin hydride (benzene, AIBN initiator), are capable of displacing tributylstannyl radicals from (4-fluorophenyltelluro)tributylstannane to afford the 4-fluorophenyltelluroalkanes 3, 8, 9.

Phenylselenides and tellurides play important roles as free-radical precursors in organic synthesis.[1–3] Recently, we reported that *ab initio* calculations using a double-ζ pseudopotential (DZP) basis set and electron correlation (MP2, QCISD)† predict that the stannyl radical undergoes reversible free-radical homolytic attack at the tellurium atom in methanetellurol with the expulsion of methyl radical [eqn. (1)].[4] Our MP2/DZP calculations give energy barriers of 28.8 and 40.3 kJ mol^{-1} for the displacement of $\cdot SnH_3$ by methyl radical and the reverse reaction respectively, while QCISD/DZP//MP2/DZP calculations give values of 26.3 and 30.1 kJ mol^{-1} for the same two reactions. Intrigued by this apparently contra-intuitive result‡ and given the increased use of aryltellurides as free-radical precursors,[2,3] we began to explore the reaction of methyl radical with phenyltellurotributyltin **1**.

$$\cdot CH_3 + H_3SnTeH \underset{\Delta E^{\ddagger} = 30.1 \text{ kJ mol}^{-1}}{\overset{\Delta E^{\ddagger} = 26.3 \text{ kJ mol}^{-1}}{\rightleftharpoons}} H_3Sn^{\cdot} + CH_3TeH \qquad (1)$$

Phenyltellurotributyltin **1** was prepared by reaction of phenyltellurocyclohexane[6] **2** with tributyltin hydride in benzene (AIBN initiator). The telluride **1** proved to be unstable, simple removal of the solvent at reduced pressure resulted in rapid decomposition. In benzene under nitrogen, **1** appears to have an indefinite lifetime. Consequently, **1** was prepared in an NMR tube in C_6D_6 (0.08 mol dm^{-3}) and characterized by ^{1}H, ^{13}C, ^{119}Sn and ^{125}Te NMR spectroscopies (Scheme 1). Specifically, **1** exhibits a singlet at δ −1.3 in the ^{119}Sn NMR spectrum with satellite coupling to ^{125}Te [$J(^{119}\text{Sn}-^{125}\text{Te})$ 2692 Hz], while the ^{125}Te NMR spectrum of **1** revealed a singlet at δ −209.4 with the expected satellite coupling to ^{117}Sn and ^{119}Sn [$J(^{117}\text{Sn}-^{125}\text{Te})$ 2578 Hz, $J(^{119}\text{Sn}-^{125}\text{Te})$ 2692 Hz].

When 1 equiv. of 4-fluorotelluroanisole[8] **3** (^{125}Te NMR, δ 350.5), tributyltin hydride (5 mol%) and AIBN (5 mol%) were introduced into the NMR tube and the colourless solution heated at 80° for 2 h, ^{119}Sn and ^{125}Te NMR spectroscopies revealed the presence of telluroanisole[8] **4** (^{125}Te NMR, δ 342.8) and 4-fluorophenyltributyltin§ **5**, in addition to starting material (Fig. 1) by comparison with authentic samples. Importantly, when **1** was heated at 80 °C in benzene either in the absence of any reagents or in the presence of 4-fluorotelluroanisole **3** and tributyltin hydride (5 mol%) with no initiator (AIBN), no reaction was observed by ^{119}Sn and ^{125}Te NMR spectroscopies after 2 h at 80 °C.



Scheme 1 Ph = C_6D_5

We postulate that formation of **4** and **5** involves homolytic substitution by methyl radical, generated by reaction of telluride **3** with tributylstannyl radical, at the tellurium atom in **1** with expulsion of further chain-carrying tributylstannyl radical (Scheme 2).

When the reaction sequence was repeated using 4-fluorophenyltributyltin **5** prepared in identical fashion to **1** using 4-fluorophenyltellurocyclohexane¶ and telluroanisole **4** as starting materials, ^{119}Sn and ^{125}Te NMR spectroscopies revealed the presence of **1** and **3**, as expected on the basis of the mechanism depicted in Scheme 2.

Given that methyl radical is capable of displacing tributylstannyl radicals through homolytic attack at tellurium, we were interested in whether or not these observations apply to alkyl radicals in general. ^{125}Te and ^{119}Sn NMR spectroscopies confirm that in similar experiments, phenyltelluroethane[9] **6**,

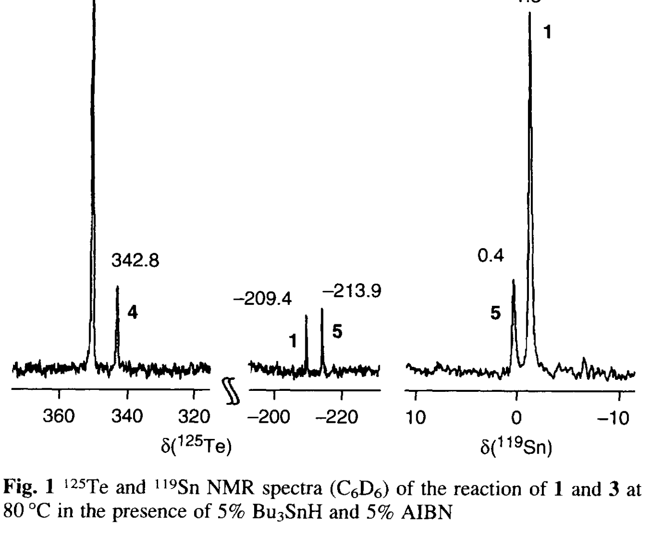
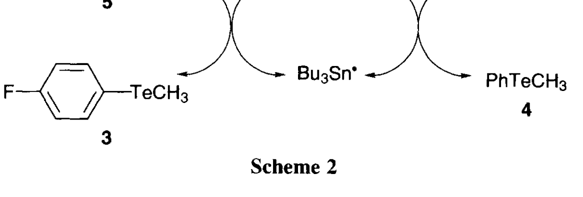


Fig. 1 ^{125}Te and ^{119}Sn NMR spectra (C_6D_6) of the reaction of **1** and **3** at 80 °C in the presence of 5% Bu_3SnH and 5% AIBN



Scheme 2

$PhTeCH_2CH_3$

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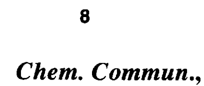

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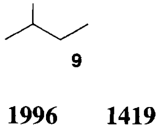

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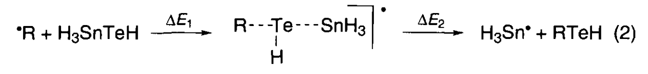
2-(phenyltelluro)butane[7] **7**, 4-fluorophenyltelluroethane¶ **8** and 2-(4-fluorophenyltelluro)butane¶ **9** react reversibly with tributylstannyl radical. Typical ^{125}Te NMR spectra for these reactions are displayed in Fig. 2.

Finally, we examined the homolytic attack of ethyl radical (a representative primary radical) and isopropyl radical (a representative secondary radical) with stannyltellurol (H$_3$SnTeH) by *ab initio* molecular-orbital calculations in the manner described previously [eqn. (2)].[4] SCF/DZP and MP2/DZP calculations predict that these reactions proceed without the involvement of intermediates; calculated transition states are displayed in Fig. 3. MP2/DZP calculations predict that displacement of stannyl radical by ethyl and isopropyl radicals should be more facile than the analogous reaction involving methyl radical, with MP2/DZP barriers of 26.7 and 22.7 kJ mol^{-1} respectively. As was observed for the reaction involving methyl, these reactions are predicted to favour slightly the formation of the alkyltellurol, with MP2/DZP-calculated exothermicities of 6.4 and 7.4 kJ mol^{-1} for the reactions involving the ethyl and isopropyl radicals respectively. Calculated SCF/DZP and MP2/DZP energy barriers are listed in Table 1.



$$\cdot R + H_3SnTeH \xrightarrow{\Delta E_1} \left[R\cdots\underset{H}{Te}\cdots SnH_3\right]^{\bullet} \xrightarrow{\Delta E_2} H_3Sn^{\bullet} + RTeH \quad (2)$$

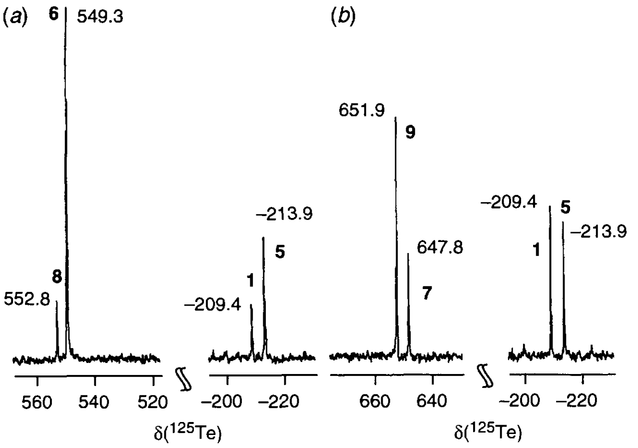


Fig. 2 ^{125}Te NMR spectra (C$_6$D$_6$) of the reactions of **5** with **6** (*a*) and **1** with **9** (*b*) at 80 °C in the presence of 5% Bu$_3$SnH and 5% AIBN

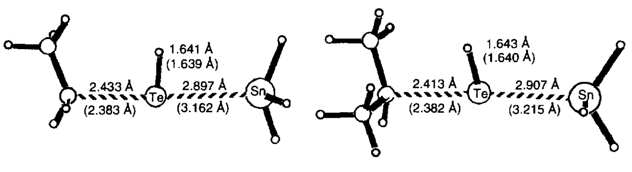


Fig. 3 MP2/DZP calculated transition states (SCF data in parentheses) for homolytic substitution by ethyl and isopropyl radicals at the tellurium atom in stannyltellurol (H$_3$SnTeH) with expulsion of stannyl radical

Table 1 SCF/DZP and MP2/DZP calculated energy barriers[a] for the forward and reverse reactions in this study [eqn. (2)]

	SCF		MP2	
Alkyl radical (R)	ΔE_1	$-\Delta E_2$	ΔE_1	$-\Delta E_2$
Me·	74.4[b]	41.1[b]	28.8[b]	40.3[b]
Et·	80.4	34.8	26.7	33.1
Pr^{i}·	88.3	30.6	22.7	30.1

[a] Energies in kJ mol^{-1}. [b] Taken from ref. 4.

In conclusion, we have demonstrated that, in agreement with *ab initio* predictions, alkyl phenyltellurides react reversibly with tributylstannyl radical in benzene under standard radical conditions. These observations are of importance to synthetic endeavours involving phenyltellurides as radical precursors.

We are currently investigating the similar process at selenium and reactions involving other chain-carrying radicals. We thank the Australian Research Council for financial support.

Footnotes

† Double-ζ pseudopotential basis set of Hay and Wadt on Sn, Te; D95 basis set on C, H. Polarization functions are included on all atoms. Basis set details are found in ref. 4 and 5.

‡ The use of alkyl halides, sulfides, selenides and tellurides as radical precursors are 'textbook' reactions usually written to afford alkyl radicals in an irreversible manner.[1–3]

§ ^{119}Sn NMR δ 0.4 [J(^{119}Sn–^{125}Te) 2656 Hz]; ^{125}Te NMR δ −213.9 [J(^{125}Te–^{117}Sn) 2526 Hz, J(^{125}Te–^{119}Sn) 2656 Hz].

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

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Received, 27th March 1996; Com. 6/02139E