O,O'-Bistributyltin Benzopinacolate (1,1,2,2-Tetraphenylethane-1,2-bisolate) as Thermal Source of Tributylstannyl Radicals

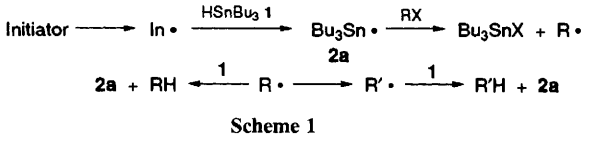
Mirosław J. Tomaszewski and John Warkentin*

Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1

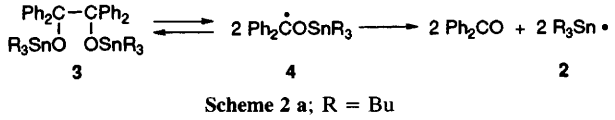
The previously unknown bistributyltin benzopinacolate was prepared by photolysis of benzophenone in the presence of bistributyltin and used for thermal formation of aryl radicals that undergo subsequent intramolecular addition to an imine bond in an *ortho*-substituent.

One of the most widely used chain-transfer reagents for organic synthesis by the radical chain mechanism[1–7] is tributylstannane **1**. A typical sequence involving the use of a halide (RX) is shown in Scheme 1. The most common problem with this scheme is chain transfer with R$^{\bullet}$, before it is converted to R'$^{\bullet}$ (by addition, cyclization, rearrangement *etc.*), because the chemistry involving the transformation of R$^{\bullet}$ to R'$^{\bullet}$ may be too slow to compete with H-abstraction from **1**, except at exceedingly low concentrations of **1**.

In order to retain the favourable halogen-abstracting properties of stannyl radicals and to avoid the premature consumption of organic radicals by **1**, other sources of stannyl radicals have been developed. In particular, Neumann and coworkers[8] prepared bistrialkyltin benzopinacolates **3b** and **3c** which afford trialkylstannyl radicals *via* homolysis and subsequent β-scission of trialkylstannyl ketyls **4** (Scheme 2). Hart and Seely[9] demonstrated the advantage of **3c** over **1** for synthetic applications. Neumann's group was not able to prepare bistributyltin benzopinacolate **3a**,[10] which is a desirable alternative to **3c** because bistributyltin is more readily available and less toxic than bistrimethyltin.† Bistrialkyltins, together with benzophenone, are the starting materials in the Neumann approach to **3**. We now report that **3a** can be prepared as a major constituent of a solution containing **3a**, benzophenone, and bistributyltin, simply by long irradiation of the reactants at 350 nm.



Scheme 1



Scheme 2 **a**; R = Bu
b; R = Et
c; R = Me

† Values of LD_{50} for oral administration to rats are: Bu_6Sn_2 87 mg kg^{-1}; Me_6Sn_2, 25 mg kg^{-1}.[11]

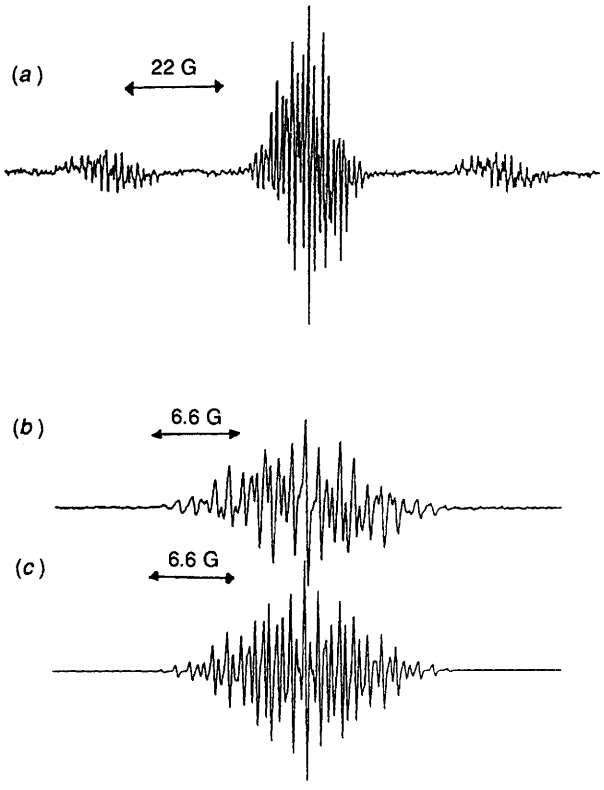
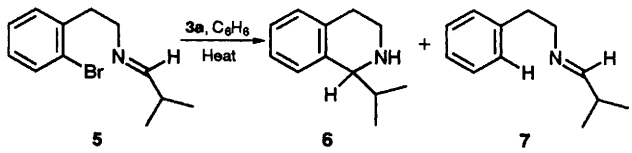


Fig. 1 (*a*) ESR spectrum of $Ph_2\dot{C}OSnBu_3$ **4a** in C_6H_{12} at 71 °C; (*b*) partial spectrum, expanded; (*c*) partial spectrum, simulated, using hyperfine coupling constants for $Ph_2\dot{C}OSnMe_3$ (ref. 13)

Irradiation of a solution of benzophenone (75.7 mg, 0.415 mmol) and Bu_6Sn_2 (120.8 mg, 0.208 mmol) in [$^2H_6$]benzene (0.4 ml) with 350 nm light (Rayonet apparatus) at 20 °C in an oxygen-free atmosphere for 24 h afforded a solution of **3a** (5.4 parts) and Bu_6Sn_2 (1 part), together with other minor components.‡ Longer irradiation did not improve the conversion, nor did a change from benzene solvent to *tert*-butylbenzene, and to cyclohexane. Attempts to use toluene as solvent were unsuccessful, presumably because triplet benzophenone abstracts H from toluene too efficiently. Comparison of the ^{119}Sn NMR spectra from irradiations at −45 °C (*tert*-butylbenzene), 20 °C (benzene) and 40 °C (benzene) indicated that there is no significant effect of temperature, within that range, on the conversion. The pinacolate **3a** was identified from its ^{119}Sn NMR, ^{13}C NMR and mass spectra, and from the results of heating a solution of **3a** in cyclohexane to 65 °C in an oxygen-free atmosphere.

Progress of the reaction of Bu_6Sn_2 with Ph_2CO was monitored by ^{119}Sn NMR spectroscopy which showed the depletion of Bu_6Sn_2 (δ −83) and the growth of a new compound with a signal at δ +73, relative to external standard Me_4Sn. The latter is close to the value reported for $Bu_3SnOCH(Me)_2$ (δ + 76).[12] The 2-dimensional heterocorrelated spectrum (^{1}H, ^{119}Sn) showed that ^{119}Sn couples to both the α- and β-CH_2 groups, with $^2J_{Sn\text{-}H} = {}^3J_{Sn\text{-}H} = 56 \pm 2$ Hz. In the ^{13}C NMR spectrum, the benzylic carbon signal of **3a** appeared at δ 88. Finally, the mass spectrum (*m/z* = 1/2 M^+, 3%) is similar to that reported for bistrimethyltin benzopinacolate,[8] which also does not afford a molecular ion but instead 1/2 M^+ (5%) as the highest *m/z*.

On warming to 65 °C in an oxygen-free atmosphere, a solution of **3a** turns salmon red in colour. That colour, which fades upon cooling, was previously observed for stannyl ketyl radicals.[8] The ESR spectrum (Fig. 1) showed a radical with $g = 2.0025 \pm 0.004$ at 56 °C, in close agreement with the *g*-value (2.0024, 31 °C) reported for the trimethylstannyl ketyl. Coupling to ^{117}Sn and ^{119}Sn (both spin 1/2) is visible (Fig. 1) and a simulation of the central portion of the spectrum, using the hyperfine coupling constants for trimethylstannyl ketyl radical,[13] reproduced the observed spectrum fairly well [Fig. 1(*c*)].



Scheme 3

Thermolysis of **3a** at 85 °C converted it, in part, to benzophenone and bistributyltin as indicated by both ^{119}Sn and ^{13}C NMR spectroscopy. There were additional products that have not been identified but presumably include those from coupling of **2a** with **4a** at the α- and ring-carbon atoms of the latter. As a test of **3a** for synthetic applications, a solution of imine **5** and **3a** was heated in benzene, (Scheme 3). At 70 °C the imine **5** was consumed in *ca.* 14 h but at 100 °C (sealed tube) the reaction was complete in less than 3 h. The ratio of products, **6** : **7** = 4 : 1, is similar to that achievable by the use of very dilute $HSnBu_3$, by means of the syringe-pump addition technique;[14] a method that is not is practical for large scale reactions.

Neumann's group reported[8] that reactions of bistrimethyltin benzopinacolate with some substrates (O_2, I_2, some RX, R_2CO, RN=NR) are much too fast to be accounted for in terms of homolysis of the pinacolate. They proposed a mechanism involving molecule-assisted homolysis to account for the high rates.[8] The initiation mechanism for the reaction of bistributyltin benzopinacolate with the imine is not known. Given that reaction of **5** with **3a** was relatively slow, initiation by homolysis is probably an adequate provisional mechanism.

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‡ Similar irradiation of a solution of bistrimethyltin and benzophenone afforded pinacolate **3c** and unreacted bistrimethyltin in 13 : 1 ratio in 7 h.

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