JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. **12**, 233–239 (1999)

Steric trends and kinetic parameters for radical reductions involving alkyldiphenyltin hydrides

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Received 5 May 1998; revised 27 June 1998; accepted 3 July 1998

ABSTRACT: Absolute rate constants and Arrhenius parameters for hydrogen atom abstraction by primary alkyl radicals from methyldiphenyl-, ethyldiphenyl-, butyldiphenyl-, *iso*propyldiphenyl-, cyclohexyldiphenyl- and (trimethylsilyl)methyldiphenyltin hydride were determined in *tert*-butylbenzene through utilization of the '5-hexenyl radical clock' reaction. At 80 °C, rate constants (k_H) for all hydrides were found to lie in the range (8.2–11.5) $\times 10^6$ $lmol^{-1}$ s^{-1}, with similar Arrhenius expressions for all reactions studied [viz. log k_H = (8.92–8.97)−(3.03–3.24)/2.3*R*T]. The nature of the alkyl substituent appears to have a subtle effect on the function of the hydride such that the order or reactivity of stannanes (RPh_2SnH) is Me > Et > Bu > *i*-Pr > *c*-Hex ≥ Me_3SiCH_2; this trend can be directly traced to steric effects operating in the transition states for hydrogen transfer from tin to carbon. The implications of these observations are discussed. Copyright © 1999 John Wiley & Sons, Ltd.

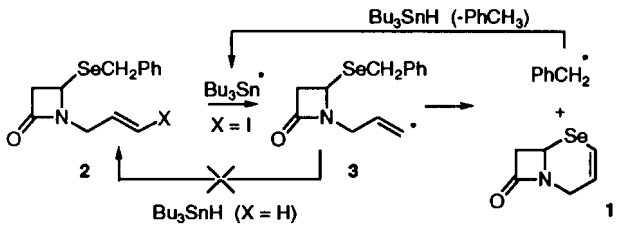
KEYWORDS: radical reduction; alkyldiphenyltin hydrides; stannane; kinetic parameters

INTRODUCTION

In free-radical chemistry, few reagents have had the same impact as tributyltin hydride.[1] As a chain-carrying reagent, tributyltin hydride is cheap, readily available and has favourable rate constants for delivery of hydrogen atom to carbon-centred and other radicals[2–6] while the corresponding stannyl radical reacts readily with a variety of free-radical precursors.[6–15] The ability to establish free-radical chain reactions of synthetic utility is a direct result of recent significant advances made in our understanding of the factors which govern radical reactivity[16–20] together with a knowledge of the important rate constants involved in the overall chain process.[1–6] Formation of carbon–carbon bonds through the use of inter- and intramolecular homolytic addition chemistry[1,21] and carbon–heteroatom bonds through the use homolytic substitution chemistry[19] are key chemical reactions of synthetic significance which directly compete with hydrogen abstraction processes from chain carriers such as tributyltin hydride.

A good example of the selective use of tributyltin hydride in synthesis is demonstrated in the recent preparation of 3,4-dehydro-8-oxo-5-selena-1-azabicyclo-[4.2.0]octane (**1**) in which precursor **2** (X = I) is reacted with tributyltin hydride presumably to afford radical **3**, which undergoes intramolecular homolytic substitution at selenium to afford the selenium-containing heterocycle **1** (Scheme 1) (R. L. Martin and C. H. Schiesser, Unpublished). Control of substrate concentration (<0.1 M) together with the judicious choice of radical precursor (iodide) allows for necessary selectivity criteria to be met (R. L. Martin and C. H. Schiesser, Unpublished). Specifically, tributylstannyl radical must react by abstraction of the iodine atom in preference to the selenide functionality in **2** (X = I), that the carbon-centred radical must react at the selenium atom in **2** in preference to hydrogen abstraction from tributyltin hydride and that the benzyl radical formed upon homolytic substitution must abstract hydrogen atom from tributyltin hydride to continue the radical chain.

Recent interest in extending the useful range of reactivity of trialkylstannanes, and in stereoselective radical reactions,[22] has seen the development of a limited number of modified stannanes.[23–26] To date, however, chiral stannanes have returned only moderate levels of



Scheme 1

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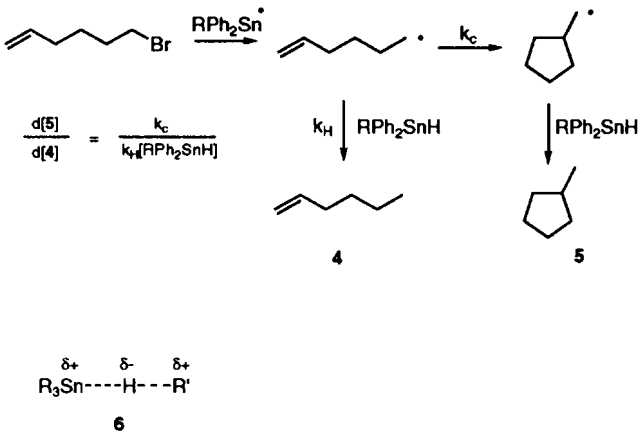
Contract/grant sponsor: Australian Research Council.

CCC 0894–3230/99/030233–07 $17.50



Scheme 2

enantioselectivity during free-radical reactions.[26] During this time, we have been engaged in work directed towards the development of homolytic substitution methods for use in synthesis.[19] Computational[27] and experimental[28] studies have led to the design of new reagents[29] and precursors[30] for use in radical chemistry. Our recent interest in the development of modified stannanes for use in radical and other chemistry required that we model hydrogen abstraction by various alkyl radicals from a series of alkylstannanes by *ab initio* molecular orbital theory.[31] These calculations (MP2/DZP; QCISD/DZP) predict that hydrogen abstraction from stannane (SnH_4) by methyl, ethyl, *iso*propyl and *tert*-butyl radicals proceed via transition states in which the attacking and leaving radicals adopt a colinear arrangement and have associated energy barriers which fall in the range of 3.3–7.6 kcal mol^{-1} (1 kcal = 4.184 kJ).[31] The predicted reactivity trend towards stannane, namely Me < primary < secondary < tertiary is in accordance with well established experimental data.[4,5]

Unfortunately, there exist few kinetic data for unsymmetrically substituted stannanes. In order to gauge the effect of alkyl substitution on the reactivity of the tin hydride, we have determined the absolute rate constants and Arrhenius parameters for a series of alkyldiphenyltin hydrides. We now report that methyldiphenyl-, ethyldiphenyl-, butyldiphenyl-, *iso*propyldiphenyl-, cyclohexyldiphenyl- and (trimethylsilyl)methyldiphenyltin hydride react with primary alkyl radicals in *tert*-butylbenzene with rate constants which fall in a narrow range, $(8.2–11.5) \times 10^6$ lmol^{-1} s^{-1} at 80 °C In addition, activation energies and log(A/lmol^{-1}s^{-1}) values have been determined to lie in the ranges 3.03–3.24 kcal mol^{-1} and 8.92–8.97, respectively. The nature of the alkyl substituent appears to have a subtle effect on the function of the hydride such that the order of reactivity of stannanes (RPh_2SnH) is Me > Et > Bu > *i*-Pr > *c*-HexE_a (kJmol^{-1}) $\geq Me_3SiCH_2$.

RESULTS AND DISCUSSION

The alkyldiphenyltin hydrides in this study were prepared by lithium aluminium hydride reduction of the corresponding fluoride. Absolute rate constants for the delivery of hydrogen atom to primary alkyl radicals were determined through application of the well established '5-hexenyl radical clock' reaction (Scheme 2).[32] Several published Arrhenius parameters exist for the ring closure of the 5-hexenyl radical.[33–37] Kinetic EPR spectroscopy provide figure s of 10.7 ± 1.0 and 9.5 ± 1.0 for the value of log(A/s^{-1}), together with activation energies of 7.8 ± 1.0 and 6.1 ± 1.0 kcal mol^{-1}.[36,37]

Competitive experiments appear to provide the most reliable expresson [Eqn 7, see below], although this expression is dependent on the quality of the rate constant (k_H) data available for competitive reduction and there appears to be some variability in published Arrhenius parameters for this reaction.[5]

In order to provide confidence in our techniques and to provide further kinetic data for the 5-hexenyl radical (clock) reaction, we chose to redetermine the Arrhenius parameters for the cyclization of the 5-hexenyl radical in the presence tributyltin hydride (Bu_3SnH), a reagent whose kinetics have been established by (primary) laser flash photolytic techniques.[5]

Calibrating the radical clock

Gas chromatography (GC) of the reaction mixture obtained when 1-bromo-5-hexene was reacted with either 1 or 10 equiv. of tributyltin hydride (0.05–0.15 M) in *tert*-butylbenzene (*ca* 5 mol% AIBN) revealed the presence of 1-hexene (**4**) and methylcyclopentane (**5**), by comparison with authentic samples. Integration of the appropriate rate equation [Eqn 1] leads to Eqn 2, which is valid under 'pseudo-first-order' conditions in stannane (i.e. 10 equiv.), or to Eqn 3 (where subscripts 0 and f denote initial and final, respectively), which is used under 'second-order conditions' (i.e. 1 equiv.).[35] In the 'second-order' reactions, overall conversions and, subsequently, the concentrations of products **4** and **5** required for Eqn 2 were determined by integration against an internal GC standard (octane). In all reactions conversions in excess of 97% (% **4** + % **5** >97%) were recorded. These GC studies also revealed the presence of small (<*ca* 1%) amounts of cyclohexane which played no role in the overall kinetic analysis.

$$d[\mathbf{5}]/d[\mathbf{4}] = k_c/(k_H[Bu_3SnH]) \quad (1)$$

$$[\mathbf{5}]/[\mathbf{4}] = k_c/(k_H[Bu_3SnH]) \quad (2)$$

$$[\mathbf{5}]_f = k_c \ln\{([Bu_3SnH]_0 + k_c/k_H/([Bu_3SnH]_f + k_c/k_H)\}/k_H \quad (3)$$

Initial reductions were carried out at three concentra-

Table 1. Rate data for the ring closure of the 5-hexen-1-yl radical in tert-butylbenzene

Temperature (°C)	Method[a]	$[Bu_3SnH]$ (M)	k_c/k_H (M)[b]	k_c ($\times 10^6$ s^{-1})
80	A	0.05	0.183	1.11
		0.10	0.185	1.11
		0.15	0.187	1.13
	B	0.05	0.186	1.13
		0.10	0.184	1.12
		0.15	0.184	1.12
60	B	0.10	0.141	0.62
70			0.170	0.88
90			0.211	1.48
100			0.228	1.83
110			0.244	2.23
120			0.292	3.03

[a] Method A: 10 equiv. of Bu_3SnH ('pseudo-first-order' condition). Method B: 1 equiv. of Bu_3SnH ('second-order' conditions).
[b] Average of three experiments.

tions (0.05, 0.1 and 0.15 M) at 80 °C under 'pseudo-first-order' and 'second-order' conditions. Applications of the appropriate integrated rate equation [Eqn 2 or 3] provide the rate constant data which are listed in Table 1; the data presented for each entry are the average of three individual experiments. The pleasing degree of convergence between the data obtained by the various methods indicates that the kinetic model (Scheme 2) is correct and that we are monitoring free-radical processes and provides confidence in our experimental techniques.

Inspection of Table 1 reveals slightly greater consistency between the data obtained using the 'second-order' technique (method B) than those obtained using 10 equiv. of the hydride. Variations in reproducibility with the latter technique are likely, as stannane addition to the olefin moiety in the starting bromide and product (1-hexene) may affect the (GC) measured product ratios. Reactions at other temperatures were carried out using 1 equiv. of tributyltin hydride (method B) at one concentration (0.1 M); the results are summarized in Table 1.

Linear regression analysis of the data presented in Table 1 provides the following (relative) Arrhenius expression (errors are expressed to 95% confidence and include random but not systematic variations)

$$\log(k_c/k_H)/\mathrm{M} = (1.06 \pm 0.18) - (2.90 \pm 0.29)/\theta \quad (4)$$

where $\theta = 2.3RT$ kcal mol^{-1}. Combining Eqn 4 with the 'best Arrhenius equation to use for the reaction of a primary alkyl radical with tributyltin hydride':[4]

$$\log k_H/\mathrm{l\ mol^{-1}s^{-1}} = (9.07 \pm 0.24) - (3.69 \pm 0.32)/\theta \quad (5)$$

leads to the following Arrhenius expression for the ring closure of the 5-hexenyl radical Eqn in *tert*-butylbenzene: (errors are expressed to 95% confidence and include random but not systematic variations)

$$\log k_c/\mathrm{s^{-1}} = (10.13 \pm 0.42) - (6.59 \pm 0.61)/\theta \quad (6)$$

Equation 6 compares very favourably with the previously determined expression:[5]

$$\log k_c/\mathrm{s^{-1}} = (10.42 \pm 0.32) - (6.85 \pm 0.42)/\theta \quad (7)$$

Given differences in solvent (e.g. *tert*-butylbenzene in this study, benzene in a previous study[33]), and for consistency, values of k_H determined in this study were calculated using Eqn 6 as the Arrhenius expression for the radical clock.

Reactions of alkyldiphenyltin hydrides

Reactions of the various alkyldiphenyltin hydrides (RPh_2SnH) with 1-bromo-5-hexene were initially performed at 80 °C under 'pseudo-first-order' and 'second-order' conditions in the same way as described for tributyltin hydride. As was observed previously, the data obtained using the 'second-order' technique (method B) proved to be superior to those obtained using method A. Results of this study summarized in Table 2.

Subtle changes in k_H can be noted on moving through the series of hydrides; the order of reactivity at 80 °C

Table 2. Selected rate data determined under second-order conditions (0.01 M) for the reactions of primary alkyl radicals with some alkyldiphenyltin hydrides in tert-butylbenzene at 80 °C

Stannane	**4** (%)	**5** (%)	k_c/k_H (M)[a]	k_H ($\times 10^6$ $lmol^{-1}$ s^{-1})
$MePh_2SnH$	38.1	61.7	0.100	11.1
$EtPh_2SnH$	28.7	71.3	0.112	9.9
$BuPh_2SnH$	27.2	71.6	0.113	9.8
i-$PrPh_2SnH$	27.4	72.8	0.120	9.3
c-$HexPh_2SnH$	23.9	74.7	0.135	8.2
$Me_3SiCH_2Ph_2SnH$	25.5	71.2	0.124	9.0

[a] Average of three experiments.

Table 3. Kinetic parameters for the reactions of some alkyldiphenyltin hydrides with primary alkyl radicals in tert-butylbenzene (60–120 °C)

Stannane	Log A ($lmol^{-1}$ s^{-1})[a]	E_a (kcal mol^{-1})[a]	k_H (80 °C)[b] ($\times 10^6$ $lmol^{-1}$ s^{-1})
Ph_3SnH	—	—	>15[c]
$MePh_2SnH$	8.94 ± 0.21	3.03 ± 0.30	11.5
$EtPh_2SnH$	8.91 ± 0.20	3.07 ± 0.20	10.2
$BuPh_2SnH$	8.95 ± 0.25	3.13 ± 0.25	10.2
i-$PrPh_2SnH$	8.95 ± 0.13	3.18 ± 0.21	9.5
c-$HexPh_2SnH$	8.92 ± 0.26	3.24 ± 0.40	8.2
$Me_3SiCH_2Ph_2SnH$	8.97 ± 0.15	3.24 ± 0.25	9.2

[a] Error limits are expressed to 95% confidence but include random and not systematic variations.
[b] Calculated from the Arrhenius parameters.
[c] Ref. 3.

is clear $MePh_2SnH > EtPh_2SnH \geq BuPh_2SnH >$ *i*-$PrPh_2SnH > Me_3SiCH_2Ph_2SnH >$ *c*-$HexPh_2SnH$, although the changes in rate constant (k_c) are small. These and other observations are discussed in more detail below.

The remaining kinetic data for the alkyldiphenyltin hydrides at temperatures other than 80 °C were obtained under 'second-order' conditions and are summarized in Table 3 together with the available data for triphenyltin hydride.[3,34] What is immediately clear from the kinetic data in Table 3 is that the alkyl substituents on the alkyltriphenyltin hydrides in this study appear to exert only a minor influence on the rate constant (k_H) and Arrhenius parameters (log A, E_a). At 80 °C, the hydrides in this study all deliver hydrogen with rate constants which fall in the narrow range $(8.2–11.5) \times 10^6$ l mol^{-1} s^{-1}, which, as expected, lie between the value for tributyltin hydride (6.1×10^6 l mol^{-1} s^{-1}) and triphenyltin hydride ($>1.5 \times 10^7$ l mol^{-1} s^{-1}).[3,34] In addition, both the entropy (log$A$) and activation energy (E_a) terms in the Arrhenius expression for each stannane are also found to lie in narrow ranges, log$A$ = 8.92–8.97 l mol^{-1} s^{-1} and E_a 3.03–3.24 kcal mol^{-1}; the log$A$ term is consistent with values determined previously for tributyltin hydride.[5]

Closer inspection of the data in Table 3 reveals the existence of a subtle trend in both activation energy and rate constant data. On moving from methyl- to ethyl-, butyl-, *iso*propyl- and cyclohexyl-substituted stannanes, decreases in rate constant (k_H) and slight increases in activation energy (E_a) can be observed, while no trend in log$A$ is apparent. We conclude, therefore, that the nature of the alkyl substituent (R) has a subtle effect on the activation energy for the reactions of the alkyldiphenyltin hydrides (RPh_2SnH) in question, which manefests itself in slight variations in rate constant (we accept that this effect is open to interpretation as the kinetic parameters listed in Table 3 have overlapping error bars). On the basis of these data, it appears that the (trimethylsilyl)-methyl substituent behaves more like a secondary alkyl substituent than a primary group.

What is the likely origin of the observed trends in E_a and k_H? It seems reasonable to postulate that the alkyl substituent is exerting either an electronic or a steric effect in the transition states (**6**) for hydrogen transfer leading to slight changes in activation energy. The former effect may well dominate if the transition state has significant polar character, while the latter effect might be important if the reacting centres in the transition state are close enough to 'feel' the steric bulk of the other.

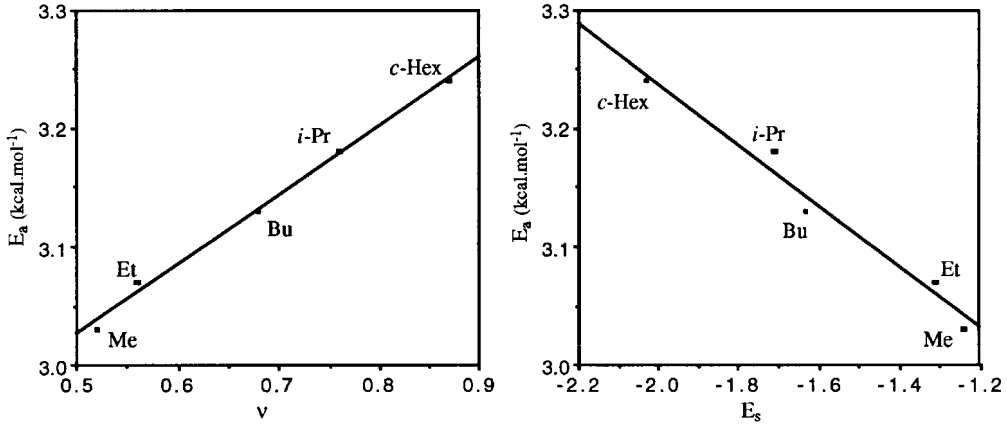


Figure 1. Correlation between activation energies (E_a, Table 3) for the reactions of the alkyldiphenyltin hydrides (RPh_2SnH) in this study with primary alkyl radicals and the Charton (left) and Taft (right) steric parameters of the alkyl substituents (R)

Our recent calculations offer insight into both of these important factors.[31] MP2/DZP calculations predict that the overall carbon–tin separation in the transition states for several alkyl radicals abstracting hydrogen from stannane (SnH_4) and trimethylstananne (Me_3SnH) lie in the narrow range 3.46–3.48 Å. In addition, only marginally polarized transition states (**6**) are predicted in which the hydrogen is '$\delta-$' and the tin is '$\delta+$'. (Mulliken charge distributions were not reported in Ref. 31) Given the relative ranking of the electron-donating ability of alkyl substituents (viz. secondary > primary > Me),[38] one would expect cyclohexyl and *iso*propyl substituents to offer greater stability to the transition state (**6**) than ethyl or butyl, which in turn would be better than methyl; the prediction, therfore, is that the activation energy (E_a) should increase in the order *c*-Hex ≤ *i*-Pr < Bu ≤ Et < Me. The *reverse is observed*, suggesting that polar effects play no significant role in transition states (**6**).

In order to provide insight into the role that steric factors play in transition states (**6**), the activation energies listed in Table 3 were correlated against both the Taft (E_s)[39] (data for Me_3SiCH_2 are unavailable) and Charton (ν)[40] (data for Me_3SiCH_2 are unavailable) steric parameter of the substituent (R), the results of which are displayed in Fig. 1. Excellent correlations are observed. We conclude, therefore, that the reactivity trends noted in this study are the direct result of subtle changes in steric crowding in the transition states involved in the transfer of hyrogen atom from the alkyldiphenyltin hydrides in this study to primary alkyl radicals.

CONCLUSIONS

Competitive experiments using tributyltin hydride have led to the calibration of the '5-hexenyl radical clock' reaction in *tert*-butylbenzene, the derived Arrhenius expression [viz. $\log k_c/s^{-1} = (10.13 \pm 0.42) - (6.59 \pm 0.61)/\theta$] being in good agreement with expressions obtained for the same reaction in other solvents. Subsequent competitive experiments using this 'clock' reaction have provided absolute rate constants and Arrhenius parameters for the hydrogen atom abstractions reactions by primary alkyl radicals from methyldiphenyl-, ethyldiphenyl-, butyldiphenyl-, *iso*propyldiphenyl-, cyclohexyldiphenyl and (trimethylsilyl)-methyldiphenyltin hydride (RPh_2SnH), which are found to lie in narrow ranges [viz. E_a = 3.03–3.24 kcal mol^{-1} and log (A/lmol^{-1} s^{-1}) = 8.92–8.97].

In addition, the subtle trend in activation energy observed as the alkyl substituent (R) is varied, namely Me < Et < Bu < *i*-Pr < *c*-Hex ≤ Me_3SiCH_2, is found to have a steric origin which is most likely due to changes in crowding in the transition state for hydrogen transfer. Clearly, then, despite the large separation between carbon and tin in the transition states (*ca* 3.5 Å) for these reactions, the reacting centres do exert an influence on each other (molecular mechanics techniques also predict that ligands on tin exert a steric influence over the alkyl radical in the transition state for hydrogen transfer).[41] Manipulation of these steric interactions through judicious choice of ligands on the tin centre should provide for modified stannanes with interesting physical properties. We are continuing to examine this interesting and useful phenonenon.

EXPERIMENTAL

NMR spectra were recorded in DMSO-d_6 unless stated otherwise. Elemental analyses were carried out by the Australian National University Microanalysis Service. All boiling-points are uncorrected.

Standard protocol A for the preparation of Alkyldiphenyltin fluorides. Methyldiphenyltin fluoride. Iodine cystals (6.1 g, 48.0 mmol) were added in portions over 2 h to a stirred cooled (0 °C) solution of methyltriphenyltin[42] (10.3 g, 28.2 mmol) in chloroform (100 ml). After warming to room temperature, the solution was stirred for a further 12 h, after which a premixed solution of acetone (50 ml) and water (50 ml) was added. Potassium fluoride (1.4 g, 24.1 mmol) was added and the mixture stirred vigorously for 3 h. The white, insoluble precipitate was collected by vacuum filtration, washed with chloroform and dried *in vacuo* to afford the title compound of sufficient purity for further use (6.2 g, 84%): m.p. 220 °C (sub.); ^{1}H NMR, δ 0.62 (3H, s), 7.3–7.7 (10H, m); ^{13}C NMR, $\delta-0.7$, 128.1, 128.8, 135.9, 144.3; ^{119}Sn NMR, $\delta-163.8$ [d, $J(^{19}F,^{119}Sn)$ = 1941 Hz]; MS (CI), *m*/*z* (relative intensity, %) 307 (1, $[M-H^+]$), 228 (100), 230 (70).

Ethyldiphenyltin fluoride. This was prepared according to the standard protocol A using ethyltriphenyltin[43] and isolated as a white solid (74%): m.p. 220 °C (sub.); ^{1}H NMR, δ 1.38 (3H, m), 1.44 (2H, m), 7.3–7.7 (10H, m); 13C NMR, δ 10.1, 11.8, 128.1, 128.7, 136.1, 144.3; ^{119}Sn NMR, $\delta-177.4$ [d, $J(^{19}F,^{119}Sn)$ = 1976 Hz]; MS (EI), *m*/*z* (relative intensity, %) 321 (2, $[M-H]^+$), 292 (100), 273 (2), 197 (34), 139 (97), 120 (20), 77 (27).

Butyldiphenyltin fluoride. This was prepared according to the standard protocol A using butyltriphenyltin[43] and isolated as a white solid (83%): m.p. 225 °C (sub.); ^{1}H NMR, δ 0.85 (3H, t, J = 7.5 Hz), 1.36 (4H, m), 1.68 (2H, m), 7.3–7.7 (10H, m); ^{13}C NMR, δ 13.6, 19.3, 26.2, 27.5, 128.0, 128.6, 136.0, 144.7; ^{119}Sn NMR, $\delta-178.8$ [d, $J(^{19}F,^{119}Sn)$ = 2092 Hz]; MS (CI), *m*/*z* (relative intensity, %) 330 (100, $[M-HF]^+$); HRMS, calculated for $C_{16}H_{19}{}^{120}Sn$ $[M-F]^+$ 331.0504, found 331.0503; analysis, calculated for $C_{16}H_{20}Sn$ C 55.1, H, 5.5, Sn 34.0, found C 54.9, H 5.2, Sn 34.0%.

Isopropyldiphenyltin fluoride. This was prepared according to the standard protocol A using *iso*-propyltriphenyltin[43] and isolated as a white solid (79%): m.p. 220 °C (sub.); ^{1}H NMR, δ 1.43 (6H, d, J = 7.5 Hz), 1.82 (1H, sept, J = 7.5 Hz), 7.3–7.7 (10H, m); ^{13}C NMR, δ 20.8, 24.6, 128.0, 128.6, 136.2, 144.3; ^{119}Sn NMR, δ−198.0 [d, J(^{19}F,^{119}Sn) = 2140 Hz]; MS (CI), *m*/*z* (relative intensity, %) 320 (16, M−CH_4]$^+$), 316 (100), 292 (25), 273 (12), 258 (60).

Cyclohexyldiphenyltin fluoride. This was prepared according to the standard protocol A using cyclohexyltriphenyltin[44] and isolated as a white solid (90%): m.p. 260 °C (sub.); ^{1}H NMR, δ 1.32 (4H, m), 1.68 (2H, m), 1.74 (4H, m), 2.01 (1H, m), 7.3–7.6 (10H, m); ^{13}C NMR, δ 26.3, 28.2, 30.2, 127.7, 128.2, 136.2; ^{119}Sn NMR, δ−202.4 [d, J(^{19}F,^{119}Sn) = 2241 Hz]; MS (EI), *m*/*z* (relative intensity, %) 375 (2, [M−H]$^+$), 356 (2), 292 (100), 273 (15), 197 (47), 139 (93), 120 (61), 83 (13), 77 (27).

(Trimethylsilyl)methyldiphenyltin fluoride. This was prepared from the coresponding chloride[45] by reaction with potassium fluoride according to the standard protocol A and isolated as a white solid (90%): m.p. 300 °C (sub.); ^{1}H NMR, δ 0.01 (9H, s), 0.36 (2H, m), 7.3–7.7 (10H, m); ^{13}C NMR, δ 1.6, 3.8, 127.9, 128.4, 136.0, 145.6; MS (EI), *m*/*z* (relative intensity, %) 364 (100, [M−CH_4]$^+$), 292 (15), 197 (83), 139 (55), 120 (64), 77 (53).

Standard protocol B for the preparation of alkyldiphenyltin hydrides Methyldiphenyltin hydride.[46]. Lithium aluminium hydride (1.25 g, 32.8 mmol) was added, under argon, in portions, to a stirred, cooled (0 °C) suspension of methyldiphenyltin fluoride (5.0 g, 16.4 mmol) in dry diethylether. The mixture was stirred for a further 3 h, then water (20 ml) was cautiously added. The solid was removed by filtration, the phases were separated and the organic layer was dried ($MgSO_4$). The solvent was removed *in vacuo* to afford the title compound as a colourless oil (3.7 g, 77%) with physical properties identical with those reported previously.[46] ^{1}H NMR (benzene-d_6), δ 0.34 (3H, s), 6.14 (1H, s), 7.1–7.2 (6H, m), 7.4–7.6 (4H, m); ^{13}C NMR (benzene-d_6) δ−11.3, 128.7, 129.0, 137.1, 138.2; ^{119}Sn NMR (benzene-d_6), δ−138.8 [d, J(^{1}H,^{119}Sn) = 1875 Hz]; MS (EI), *m*/*z* (relative intensity, %) 288 (66, [M−H_2]$^+$), 273 (5), 197 (100), 120 (82), 77 (8).

Ethyldiphenyltin hydride. This was prepared according to the standard protocol B using ethyldiphenyltin fluoride and isolated as a colourless oil (93%): ^{1}H NMR (benzene-d_6), δ 1.19–1.38 5H, m), 6.30 (1H, s), 7.1–7.2 (6H, m), 7.4–7.6 (4H, m); ^{13}C NMR (benzene-d_6), δ 2.0, 11.2, 128.4, 128.7, 137.2, 137.7; ^{119}Sn NMR (benzene-d_6), δ−130.2 [d, J(^{1}H,^{119}Sn) = 1765 Hz]; MS (EI), *m*/*z* (relative intensity, %) 303 (2, [M−H]$^+$), 274 (100), 226 (3), 197 (81), 120 (65), 77 (13), HRMS, calculated for $C_{14}H_{15}Sn$ 303.0192, found 303.0182.

Butyldiphenyltin hydride. This was prepared according to the standard protocol B using butyldiphenyltin fluoride and isolated as a colourless oil (95%): ^{1}H NMR (benzene-d_6), δ 0.77 (3H, t, J = 7.5 Hz), 1.24 (4H, m), 1.54 (2H, m), 6.29 (1H, s), 7.1–7.2 (6H, m), 7.4–7.6 (4H, m); ^{13}C NMR (benzene-d_6), δ−0.2, 13.6, 27.4, 28.7, 128.5, 129.1, 137.2, 137.9; ^{119}Sn NMR (benzene-d_6), δ−136.0 [d, J(^{1}H,^{119}Sn) = 1798 Hz]; MS (EI), *m*/*z* (relative intensity, %) 331 (14, [M−H]$^+$), 274 (49), 197 (100), 120 (45), 77 (2).

Isopropyldiphenyltin hydride. This was prepared according to the standard protocol B using *iso*-propyldiphenyltin fluoride and isolated as a colourless oil (97%): ^{1}H NMR (benzene-d_6), δ 1.27 (6H, d, J = 8.0 Hz), 1.67 (1H, sept, J = 8.0 Hz), 6.37 (1H, s), 7.1–7.2 (6H, m), 7.4–7.6 (4H, m); ^{13}C NMR (benzene-d_6), δ 15.9, 22.2, 128.8, 129.0, 137.7, 138.1; ^{119}Sn NMR (benzene-d_6), δ−122.7 [d, J(^{1}H,^{119}Sn) = 1731 Hz]; MS (EI), *m*/*z* (relative intensity, %) 317 (23, [M−H]$^+$), 274 (29), 197 (100), 120 (46), 77 (2).

Cyclohexyldiphenyltin hydride. This was prepared according to the standard protocol B using cyclohexyldiphenyltin fluoride and isolated as a colourless oil (79%): ^{1}H NMR (benzene-d_6), δ 1.19 (4H, m), 1.50–1.60 (6H, m), 1.83 (1H, m), 6.38 (1H, s), 7.1–7.2 (6H, m), 7.4–7.6 (4H, m); ^{13}C NMR (benzene-d_6), δ 26.7, 27.8, 28.5, 31.9, 128.4, 128.6, 137.4, 137.9; ^{119}Sn NMR (benzene-d_6), δ−136.9 [d, J(^{1}H,^{119}Sn) = 1706 Hz]. MS (EI), *m*/*z* (relative intensity, %) 356 (23, [M−H_2]$^+$), 274 (88), 197 (100), 120 (83), 77 (13); analysis, calculated for $C_{18}H_{22}Sn$ C 60.6, H 6.2, found C 60.5, H 6.2%.

(Trimethylsilyl)methyldiphenyltin hydride. This was prepared according to the standard protocol B using (trimethylsilyl)diphenyltin fluoride and isolated as a colourless oil (52%): ^{1}H NMR (benzene-d_6), δ−0.12 (9H, s), 0.10 (2H, s), 5.23 (1H, s), 7.1–7.2 (6H, m), 7.4–7.6 (4H, m); ^{13}C NMR (benzene-d_6), δ−6.2, 0.9, 128.4, 128.7, 136.9, 138.5; ^{119}Sn NMR (benzene-d_6), δ−130.8 [d, J(^{1}H,^{119}Sn) = 1753 Hz]; MS (EI), *m*/*z* (relative intensity, %) 361 (23, [M−H]$^+$), 274 (43), 269 (100), 197 (78), 120 (54), 77 (10); analysis, calculated for $C_{16}H_{22}SiSn$ C 53.2, H 6.1, Sn 32.9, Found C 53.0, H 6.2, Sn 32.6%.

Typical kinetic experiment (method A). An aliquot (100 µl) of a standard solution (0.05–0.15 M) of the stannane in *tert*-butylbenzene was placed in a small Pyrex tube, 1-bromo-5-hexene (*ca* 0.1 equiv.) and AIBN (*ca* 1 crystal) were added and the solution was degassed by the usual freeze–thaw technique, before being sealed

under vacuum. After being thermolysed in an oil-bath at the required temperature, the solution was analysed by GC.

Typical kinetic experiment (method B). An aliquot (100 μl) of a standard solution (0.05–0.15 M) of the stannane, 1-bromo-5-hexene (1.0 equiv.) and AIBN (*ca* 2 mol%) in *tert*-butylbenzene were placed in a small Pyrex tube and the solution was degassed by the usual freeze–thaw technique, before being sealed under vacuum. After being thermolysed in an oil-bath at the required temperature, the solution was analysed by GC.

Acknowledgements

We thank the Australian Research Council for financial support and the award of an Australian Postgraduate Award to D.J.H.

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