

## Ready Oxidative Addition of an Alkyl or Aryl Halide to a Tin(II) Alkyl or Amide; Evidence for a Free-radical Pathway†

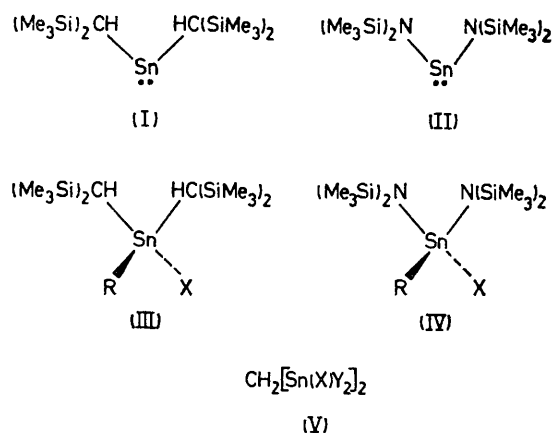
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**Summary** The addition of an alkyl or phenyl halide RX to  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  (X = Cl, Br, or I) or  $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$  (X = Br or I) in n-hexane at 20 °C readily affords the 1:1-adduct (or 1:2-adduct for  $\text{RX} = \text{CH}_2\text{Br}_2$  or  $\text{CH}_2\text{I}_2$ ) which shows two sets of diastereotopically distinct  $\text{Me}_3\text{Si}$  groups for  $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2(\text{X})\text{R}$  but not the nitrogen analogue; optical-activity and e.s.r. data suggest a free-radical mechanism with  $\cdot\text{SnY}_2(\text{X})$  and  $\text{R}\cdot$  as intermediates [ $\text{Y} = (\text{Me}_3\text{Si})_2\text{CH}$  or  $(\text{Me}_3\text{Si})_2\text{N}$ ].

BOTH the tin(II) alkyl (I)<sup>1</sup> and amide (II)<sup>2,3</sup> are monomeric in benzene or cyclohexane solution.<sup>1,2</sup> The metal atom is therefore not only co-ordinatively unsaturated but also in a low oxidation state ( $n - 2$ , where  $n$  is the most stable oxidation state). Such  $s^2$  compounds are thus potential substrates to give  $d^{10}$  adducts, having the metal in the oxidation state  $n$ . Reactions of such type are known for certain  $\text{Sn}^{\text{II}}$  compounds;<sup>2-8</sup>  $\text{SnCl}_2$  insertions are especially well studied.

We now report that (i) an alkyl or, surprisingly, an aryl halide RX reacts with (I) or (II) under mild conditions to give the 1:1-adduct (III) or (IV); (ii) for (I) or (II) and  $\text{CH}_2\text{X}_2$  (X = Br or I) a 2:1-adduct (V) [ $\text{Y} = (\text{Me}_3\text{Si})_2\text{CH}$  or  $\text{N}(\text{SiMe}_3)_2$ ] is formed; (iii) relative reactivities for oxidative addition are (I) > (II) and  $\text{RI} > \text{RBr} > \text{RCl}$ ; (iv) the  $^1\text{H}$  or  $^{13}\text{C}$  n.m.r. spectra of (III) and (IV) show interesting differences which suggest that the compounds, although iso-electronic, are not isostructural; and (v) e.s.r. spectra [for the system (I)-EtBr or (I)-Pr<sup>n</sup>Br] and optical activity data [for (I), which with (+)- $n\text{-C}_6\text{H}_{13}(\text{Me})\text{CHCl}$  gives the racemate (III)] are consistent with a radical mechanism, probably of non-chain type with  $\cdot\text{SnY}_2(\text{X})$  [ $\text{Y} = (\text{Me}_3\text{Si})_2\text{CH}$ ] as an

intermediate. Items (i)–(iv) are further illustrated in the Table. It had previously been shown that either pyrolysis<sup>4a</sup> or irradiation<sup>4b</sup> of di-n-butyltin(IV) polymer and an alkyl halide RX gives  $\text{SnBu}_2(\text{X})\text{R}$  and the proposal that RX is a trapping agent for the transient  $\text{SnBu}_2$  now seems very plausible.



We assign the 1:1-doublets found in the  $^1\text{H}$  n.m.r. spectra of compounds (III) at  $\tau$  ca. 9.9 to the two magnetically distinct diastereotopic  $\text{Me}_3\text{Si}$  environments, a result of the prochiral stereochemically rigid tetrahedral tin centre. Previous examples of diastereotopy in organotin compounds seem to have been solely with types  $\text{R}^1\text{R}^2\text{R}^3\text{MM}'\text{A}_2\text{X}$  (the groups A are diastereotopic) in which there is one chiral centre ( $\text{MM}' = \text{CSn}$  or  $\text{SnC}$ ).<sup>9</sup> The collapse of the doublet

† No reprints available.

TABLE

Examples of  $s^2 \rightarrow d^{10}$  oxidative addition reactions,<sup>a</sup> and comments on the products

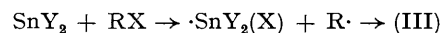
Substrate	Reagents Halide	Time (h) for complete reaction <sup>b</sup>	M.p. (°C)	Products (III) or (IV) <sup>c</sup> Nature of Me <sub>3</sub> Si <sup>1</sup> H (or <sup>13</sup> C) n.m.r. signal <sup>d</sup>
(I)	EtI	< 0.01	76—77	doublet <sup>e</sup> (doublet)
(I)	CH <sub>2</sub> Br <sub>2</sub>	ca. 1	156—158	doublet
(I)	Bu <sup>+</sup> Cl	ca. 1	(b.p. 130 °C at 0.001 mmHg)	doublet <sup>e</sup>
(I)	PhCl	ca. 80	(b.p. 124 °C at 0.001 mmHg)	doublet
(II)	MeI	ca. 0.2	78—84	singlet
(II)	MeBr	ca. 3	36—37	singlet <sup>f</sup>
(II)	Bu <sup>+</sup> Cl	g	—	—
(II)	PhI	ca. 4	(b.p. 105 °C at 0.001 mmHg)	singlet

<sup>a</sup> Other organic Sn<sup>II</sup> examples are for (a) (I) with [Mo(CO)<sub>3</sub>( $\eta$ -C<sub>6</sub>H<sub>5</sub>)X] (X = H or Me), [PtCl(PEt<sub>3</sub>)<sub>2</sub>],<sup>5</sup> MeI, or (Me<sub>3</sub>Si)<sub>2</sub>CHCl;<sup>6</sup> (b) (II) with [Fe(CO)<sub>2</sub>( $\eta$ -C<sub>6</sub>H<sub>5</sub>)Me];<sup>2</sup> (c) Sn( $\eta$ -C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> with RI (R = Me or CH<sub>2</sub>I), RBr (R = CH<sub>2</sub>:CHCH<sub>2</sub> or EtO<sub>2</sub>CCH<sub>2</sub>),<sup>7</sup> or [Fe<sub>2</sub>(CO)<sub>9</sub>];<sup>8</sup> (d) Sn(acac)<sub>2</sub> with RI (R = Me or Pr) or RBr (R = PhCH<sub>2</sub>, Ph<sub>3</sub>C, CH<sub>2</sub>:CHCH<sub>2</sub>, or EtO<sub>2</sub>CCH<sub>2</sub>).<sup>7</sup> <sup>b</sup> These refer to (I) or (II) (1 mol) and the halide (1 mol) in n-C<sub>6</sub>H<sub>14</sub> at 20 °C under argon. <sup>c</sup> All compounds (III)—(V) gave satisfactory microanalytical, i.r. [ $\nu$ (Sn—C), 460—600 cm<sup>-1</sup>,  $\nu$ (SnN<sub>2</sub>) ca. 372 ± 2 and 412 ± 2 cm<sup>-1</sup>, and  $\nu$ (Sn—Cl), 328 ± 3 cm<sup>-1</sup>], <sup>1</sup>H n.m.r., and mass [(parent—Me)<sup>+</sup> as highest peak] spectral data. <sup>d</sup> In C<sub>6</sub>H<sub>6</sub> (R = alkyl) or CH<sub>2</sub>Cl<sub>2</sub>. <sup>e</sup> Two sharp resonances of equal intensity separated by 5—10 Hz (at 60 MHz); no sign of coalescence up to 100 °C, but signal collapsed to singlet upon addition of (CD<sub>3</sub>)<sub>2</sub>SO or C<sub>6</sub>D<sub>6</sub>N. <sup>f</sup> No sign of splitting when the sample in PhCD<sub>3</sub> was cooled to -65 °C. <sup>g</sup> Similarly there was no reaction between (II) and PrCl, Bu<sup>n</sup>Cl, (Me<sub>3</sub>Si)<sub>2</sub>CHCl or PhCl at 20 or 80 °C.

upon addition of strong base is attributed to formation of a stereochemically non-rigid five-co-ordinate tin(IV) adduct (see also ref. 9), in which  $\nu$ (Sn—Cl) is at 318 cm<sup>-1</sup>. The singlet observed in the related amides (IV) arises either because of planarity at nitrogen or a very low N-inversion barrier.

The e.s.r. data on the reactions of (I) with an alkyl halide RBr relate to (a) R = Et or Pr<sup>n</sup> in benzene at room temperature when in the presence of the spin-trap nitrosodurene (ArNO•) a strong signal of the nitroxide Ar(R)NO was observed, and (b) R = Et in hexane at -60 °C when a broad singlet ( $g = 2.0214$ ) was obtained which decayed

as the reaction went to completion, and is attributed to  $\cdot$ SnY<sub>2</sub>(Br) rather than  $\cdot$ SnY<sub>2</sub>(R) [Y = (Me<sub>3</sub>Si)<sub>2</sub>CH] (cf. ref. 10; for  $\cdot$ SnY<sub>3</sub>  $g = 2.0094$ ). We thus favour a mechanism similar to that proposed for the  $d^{10} \rightarrow d^8$  oxidative addition of methyl iodide to [Pt(PPh<sub>3</sub>)<sub>3</sub>].<sup>11</sup>



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