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Preliminary Communication

Hydrostannation and hydrostannolysis by diorganotin hydrides R_2SnXH (X = halide, carboxylate, sulphonate, etc.)

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Abstract

Diorganotin halide hydrides or carboxylate hydrides, R_2SnXH, will bring about the hydrostannolysis of alkyl halides, or the hydrostannation of alkynes or of carbonyl compounds at or below room temperature. The reactions show different chemo-, regio-, and stereo-selectivities from those involving tributyltin hydride.

Key words: Tin; Hydrostannation; Hydrostannolysis; Free radical; Hydride

Diorganotin dihydrides, R_2SnH_2, readily undergo disproportion on mixing with dialkyltin(IV) compounds R_2SnX_2 (X = halide, carboxylate, sulphonate etc.) to give, in equilibrium, new hydrides R_2SnXH, with different properties from those of the parent dihydrides or of more familiar trialkyltin hydrides, R_3SnH [1,2]. In particular, these new hydrides decompose at room temperature, more or less readily depending on the nature of X, by a radical chain mechanism [3], to give dihydrogen and the corresponding tetraorganodistannane, XR_2SnSnR_2X [2,4]. By addition of a suitable substrate, the intermediate stannyl radicals can be diverted into hydrostannation or hydrostannolysis [3]. These reactions with the reagents R_2SnXH might be expected to show different rates, and different chemo-, regio-, and stereo-selectivities from those involving trialkyltin hydrides, and thus may be useful in organic synthetic procedures. We report here a study of the properties of some of these hydrides R_2SnXH in the hydrostannolysis of organic halides and the hydrostannation of alkynes and carbonyl compounds.

The elementary steps in homolytic hydrostannolysis and homolytic hydrostannation are shown in eqns. (1)–(6) [5].

Initiation

$$\xrightarrow{R_i} \mathrm{Sn}\bullet \tag{1}$$

Propagation

$$\left.\begin{array}{l} \mathrm{Sn}\bullet + \mathrm{Rz} \xrightarrow{k_p} \mathrm{SnZ} + \mathrm{R}\bullet \\ \mathrm{R}\bullet + \mathrm{SnH} \longrightarrow \mathrm{RH} + \mathrm{Sn}\bullet \end{array}\right\} \tag{2}$$

OR

$$\left.\begin{array}{l} \mathrm{Sn}\bullet + \mathrm{Y{=}Z} \longrightarrow \mathrm{SnYZ}\bullet \\ \mathrm{SnYZ}\bullet + \mathrm{SnH} \longrightarrow \mathrm{SnYZH} + \mathrm{Sn}\bullet \end{array}\right\} \tag{3}$$

Termination

$$2\mathrm{Sn}\bullet \xrightarrow{2k_t} \mathrm{Products} \tag{4}$$

$$\left.\begin{array}{l} 2\mathrm{R}\bullet \longrightarrow \mathrm{Products} \\ \mathrm{R}\bullet + \mathrm{Sn}\bullet \longrightarrow \mathrm{Products} \end{array}\right\} \tag{5}$$

OR

$$\left.\begin{array}{l} 2\mathrm{SnYZ}\bullet \longrightarrow \mathrm{Products} \\ \mathrm{SnYZ}\bullet + \mathrm{Sn}\bullet \longrightarrow \mathrm{Products} \end{array}\right\} \tag{6}$$

The overall rate of reaction will depend on the rates of these individual steps. For example if the first propagation step of the hydrostannolysis reaction is slower than the second, and we make the simplifying assumption that termination only occurs during eqn. (4), the overall rate will be given by eqn. (7).

$$-\mathrm{d}[\mathrm{RZ}]/\mathrm{d}t = k_p[\mathrm{RZ}](R_i/2k_t)^{1/2} \tag{7}$$

Benzyl chloride is not reduced by tributyltin hydride at room temperature, and the reaction requires intitiation with AIBN at 80°C. The reduction by Bu_2SnHCl requires no initiator, and the reaction is complete at room temperature in 3–3.5 h; similarly $Bu_2Sn(OCOMe)H$, $Bu_2Sn(OCOPh)H$, and $Bu_2Sn(OCOCF_2Cl)H$ react to completion at 25°C in 3–4 h, 2.5 h, and 1.5 h respectively. With the carboxylate hydrides and the sulphonate hydride, which undergo spontaneous decomposition at room temperature, the initiation is probably provided largely though this decomposition process, which we have suggested to be

$$\mathrm{Bu_2SnH_2} + \mathrm{Bu_2SnX_2} \longrightarrow \mathrm{Bu_2SnH_2^{\bullet+}} + \mathrm{Bu_2SnX_2^{\bullet-}} \tag{8}$$

$$\mathrm{Bu_2SnX_2^{\bullet-}} \longrightarrow \mathrm{X^-} + \mathrm{Bu_2SnX}\bullet \tag{9}$$

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TABLE 1. Relative rate constants (k_B/k_A) for the reaction of organic halides with stannyl radicals

A	B	Bu_3SnH	Bu_2SnH_2	Bu_2SnClH	$Bu_2Sn(OAc)H$	$Bu_2Sn(OMes)H$ [a]
$PhCH_2Br$	CCl_4	2.12	0.47	0.43	0.19	0.14
$PhCH_2Br$	$BrCH_2CO_2Et$	1.49 [b]	0.70	0.73	0.73	0.54
$PhCH_2Br$	$C_{12}H_{25}I$	2.57 [c]	1.37 [d]	1.52 [d]	1.56	1.98

[a] OMes = methanesulphonate; [b] 1 h, [c] 3 h; [d] 30 min.

With the chloride hydride, which is more stable at room temperature, the substrate which is being reduced may also be involved in the electron transfer.

Table 1 shows the products from competitive reductions of mixtures of two of the components $PhCH_2Br$, $BrCH_2CO_2Et$, and $C_{12}H_{25}I$; all these reactions occur rapidly (< 5 min) at room temperature unless otherwise noted.

The intermediate reaction rates that are sometimes observed with Bu_2SnH_2 must be interpreted with caution because the reaction produces Bu_2SnXH, which will be in equilibrium with Bu_2SnH_2 and Bu_2SnX_2, and these components may become involved in the later stages of the reaction.

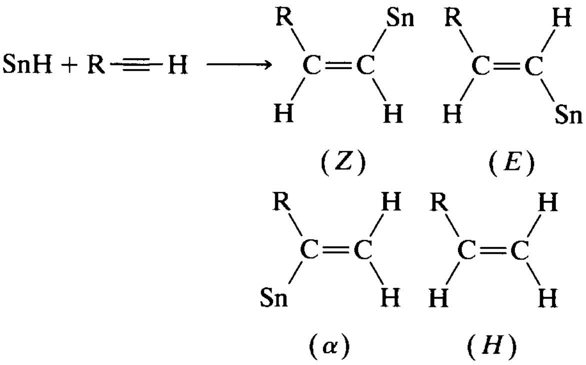
The selectivity between the two halides is determined by the rates of the propagation step in which the tin radical abstracts halogen from the halide (eqn. (2)). Steric factors are unlikely to be important with these substrates, and the selectivity may reflect the ability of the alkyl group to stabilise a negative charge in the canonical form of the transition state $Sn^{+}X{\bullet}R^{-\bullet}$.

The reactivity of a selection of tin hydrides towards acetophenone at room temperature is illustrated in Table 2.

No reaction occurs between tributyltin hydride or dibutyltin dihydride and acetophenone at room temperature, but the hydrides Bu_2SnXH do react in a few hours to give the tin derivative of 1-phenylethanol (eqn. (10)), and the sequence of reactivity correlates with the rate of homolytic decomposition at room temperature. It seems likely that the principal initiation process involves spontaneous decomposition of the hydride (eqns. (8) and (9)) and does not involve the carbonyl compound.

$$PhCOMe + Bu_2SnXH \longrightarrow PhMeCHOSnBu_2X \qquad (10)$$

Organotin hydrides can react with alkynes to give four types of products (eqn. (11)) which we designate as *Z*, *E*, *α*, and *H*.



(11)

No reaction is apparent between tributyltin hydride or dibutyltin dihydride and 2-methyl-3-butyne-2-ol or 3,3-dimethyl-1-butyne at room temperature. Reaction can be induced with AIBN at 75–80°C and gives initially a preponderance of the *Z* adduct, but as the reaction proceeds, this isomerises, and after *ca.* 2 h the ratio *Z*/*E* is 50:50 and 0:100, respectively. The hydrides Bu_2SnXH react in a few hours at room temperature, to give the products shown in Table 3; at this temperature the products are stereochemically stable.

TABLE 2. Percentage yields in the hydrostannation of acetophenone

Time (h)	Bu_3SnH	Bu_2SnH_2	Bu_2SnClH	$Bu_2Sn(OAc)H$	$Bu_2Sn(OCOR)H$ [a]	$Bu_2Sn(OMes)H$ [b]
1	0	0		46		69
2	0	0	51	68	47	81
3	0	0	84		61 [c]	

[a] R = PhCH(OMe); the 1-phenylethanol obtained from reduction with the hydride prepared from the optically active dicarboxylate, $[\alpha]_D + 54°$, was inactive within the experimental error.

[b] OMes = methanesulphonate.

[c] 71% after 20 h.

TABLE 3. Percentages of stereoisomeric alkenes obtained from the hydrostannation of alkynes

Alkyne		Bu_3SnH	Bu_2SnClH	$Bu_2Sn(OAc)H$
$Me_2C(OH)C{\equiv}CH$	*Z*	40	67 [b]	67
	E	40	0 [b]	33
	α	20	33 [b]	0
$Me_3CC{\equiv}CH$	*Z*	0	0 [c]	0
	E	100	90 [c]	0
	H	0	10 [c]	100

[a] PhMe, AIBN, 80°C, 3 h.
[b] PhMe, AIBN, 25°C, 2 h.
[c] PhMe, 25°C, 2h.

Thus, whereas hydrostannolysis and hydrostannation reactions with tributyltin hydride usually need elevated temperatures and the addition of a radical initiator, the hydrides R_2SnXH will bring about similar reactions at or below room temperature in the absence of an added initiator, and can provide alternative chemo-, regio-, and stereo-selectivities. Further, the tin can be recovered as the insoluble dibutyltin oxide, which is easily removed, has a low toxicity, and can be recycled.

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