equation $1/[([B_0] - [A_0])\ln([BA_0]/[AB_0])] = kt$, where [A] = [substrate] and [B] = [complexed ligand] or vice versa. All rates involved at least 10 samplings and gave correlation coefficients of 0.996 or better.

Reaction Products. In a typical procedure the flask used for kinetic runs termostated at 60 °C was charged with 63 mmol of the appropriate inorganic salt KY, with 15 mL of a 53% aqueous solution of KOH, and with 10 mL of a benzene (or chlorobenzene) solution of substrate **3** (1.2 M), of catalyst **1a** (0.025 M) or **2** (0.05 M), and of *n*-decane (0.4 M) (as GLC internal standard). The heterogeneous mixture was stirred for 1–11 h. The progress of the reaction was monitored by GLC analysis (50 cm × 1/8 in. in OV-101-5% on Chromosorb GHP 100–120 mesh column, in a program temperature from 50 to 150 °C). At 98–100% conversion the mass balance was ≥95%, except for the reactions with SCN^-, for which it was ≥81%, the remainder being tars. The distribution of reaction products for various nucleophilic substitutions is reported in Table V.

Reaction of Organotin Hydrides with Acid Chlorides. Mechanism of Aldehyde and Ester Formation[1]

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Abstract: Tri-*n*-butyltin hydride reacts with acid chloride, RCOCl, spontaneously at ambient temperatures to form *n*-Bu_3SnCl, RCHO, $RC(O)OCH_2R$, and a number of minor products. The reaction is not a radical chain process, nor are radicals involved as intermediates. The initial products are *n*-Bu_3SnCl and RCHO; it is not known whether these are formed in a direct reaction between *n*-Bu_3SnH and RCOCl or via an unstable chloroalkoxytin species, *n*-$Bu_3SnOCHClR$. The remaining products are formed by subsequent reactions of the aldehyde. Thus, the alkoxytin species, *n*-Bu_3SnOCH_2R, is formed from aldehyde and tin hydride. This can react further with RCOCl to form the ester $RC(O)OCH_2R$, with RCHO to form *n*-$Bu_3SnOCH(R)OCH_2R$, and with *n*-Bu_3SnH to form RCH_2OH. The aldehyde can also react with RCOCl to form the α'-chloro ester, RC(O)OCHClR.

Triorganotin hydrides react spontaneously at ambient temperatures with many acid chlorides to form the corresponding triorganotin chloride, aldehyde, and ester as the major products.[4-11]

$$R'_3SnH + RCOCl \rightarrow R'_3SnCl + RCHO + RC(O)OCH_2R \tag{1}$$

Surprisingly, the relative yields of aldehyde and ester have been found to depend not only on the structure of the acid chloride but also on the experimental conditions, e.g., whether or not a solvent is employed.

A rather detailed mechanistic study of the tri-*n*-butyltin hydride/acid chloride reaction has been carried out by Kuivila and Walsh.[9,10] It was concluded that both aldehyde and ester were produced by free-radical chain processes involving acyl radicals as intermediates. The formation of aldehyde was suggested to be mechanistically analogous to the formation of alkane in the tin hydride/alkyl halide reaction,[12]

$$n\text{-}Bu_3Sn\cdot + RCOCl \rightarrow n\text{-}Bu_3SnCl + RC{=}O \tag{2}$$

$$R\dot{C}{=}O + n\text{-}Bu_3SnH \rightarrow RCHO + n\text{-}Bu_3Sn\cdot \tag{3}$$

Four pathways for the formation of ester were considered,[10] and it was concluded that the most probable involved acyl radical addition to the aldehyde formed in reaction 3.

$$R\dot{C}{=}O + RCHO \rightarrow RC(O)O\dot{C}HR \tag{4}$$

$$RC(O)O\dot{C}HR + n\text{-}Bu_3SnH \rightarrow RC(O)OCH_2R + n\text{-}Bu_3Sn\cdot \tag{5}$$

In a preliminary communication[13] we presented evidence that free radicals are not involved in the spontaneous reaction of tri-*n*-butyltin hydride with at least some acid chlorides and that if free radicals are deliberately generated in the system, the nature of the products may be changed. For example, in the *n*-Bu_3SnH/pivaloyl chloride reaction, the main product of the spontaneous reaction was pivalaldehyde and the main product of the radical initiated reaction was isobutane.

$$n\text{-}Bu_3SnH + Me_3CCOCl \xrightarrow{\text{spontaneous}} n\text{-}Bu_3SnCl + Me_3CCHO$$

$$\xrightarrow{\text{initiated}} n\text{-}Bu_3SnCl + Me_3CH + CO \tag{6}$$

In the present paper we amplify our earlier report.[13] Additional data on the spontaneous reaction serves to confirm the nonradical mechanism of aldehyde formation. Ester is also shown to be produced by a nonradical process.

Results

To distinguish between radical and nonradical processes we have studied the products and kinetics of the spontaneous and of the

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Table I. Major Products of the Reaction of 0.6 M n-Bu$_3$SnH with 0.6 M Me$_3$CCOCl in n-Octane[a]

initiator or inhibitor, (concn, M)	T, °C	reaction time, h	[Me$_3$CH], M	[Me$_3$CCHO], M	[Me$_3$CC(O)OCH$_2$CMe$_3$], M
none	25	26	0.007	0.551	0.007
none	60	9	0.023	0.624	0.006
galvinoxyl (0.06)	25	26	0.000	0.497	0.004
galvinoxyl (0.06)	60	9	0.000	0.536	0.015
Me$_3$CONNOCMe$_3$ (0.01)	60	9	0.543	0.055	0.003
azocumene (0.01)	60	13	0.554	0.072	0.001

[a] Main reactants measured by volume, estimated error $\leqslant 5\%$. Products determined by GC analysis. Trace amounts of Me$_3$CCH$_2$OH and Me$_3$CC(O)OCHClCMe$_3$ were also formed.

radical-initiated reactions between tri-n-butyltin hydride and a few carefully selected acid chlorides. Two of the acid chlorides studied were chosen because the corresponding acyl radicals were known to undergo relatively rapid and characteristic unimolecular reactions which might be expected to compete with the potential alternative bimolecular processes, reactions 3 and 4.[14]

Formation of Pivaloyl Radicals in the Presence of n-Bu$_3$SnD. The decarbonylation of acyl radicals serves as a useful probe for their involvement in chemical reactions. Kuivila and Walsh[9] attempted to exploit this characteristic feature of acyl radical chemistry. However, only triphenylacetyl chloride was found to yield any carbon monoxide, and then only small amounts under conditions specifically designed to encourage decarbonylation (T = 100–110 °C, slow addition of hydride). When kinetic data later became available this result became rather surprising. Thus, at room temperature the rate constant for reaction 7, decarbonylation

$$\mathrm{Me_3C\dot{C}{=}O \rightarrow Me_3\dot{C} + CO} \tag{7}$$

of the pivaloyl radical, is ca. 1×10^5 s^{-1},[15] while acyl radicals yielding resonance stabilized alkyls decarbonylate even more rapidly.[16-18] Simple primary, secondary, and tertiary alkyl radicals abstract hydrogen from n-Bu$_3$SnH with rate constants of ca. 2×10^6 M^{-1} s^{-1}.[19,20] Taken together, the Kuivila and Walsh data[9] plus these kinetic data[15-20] imply either that acyl radicals are not involved in the tin hydride/acid chloride reaction or that acyl radicals are extremely reactive toward tin hydride.[21]

As we have previously reported[13] acyl radicals are not involved in at least some of these reactions because the decarbonylation of pivaloyl competes very effectively with their attack upon tin hydride or deuteride. For example,[13] heating a mixture containing 0.25 M Me$_3$CONNOCMe$_3$ and 1 M n-Bu$_3$SnD in 10 M Me$_3$CCHO to 50 °C for 16 h (ca. 8 half-lives of the hyponitrite) gave 1.5 M isobutane containing ca. 16% Me$_3$CD. However, there was no detectable incorporation of deuterium into the remaining aldehyde. It is clear that pivaloyl radicals were produced and that they underwent decarbonylation in preference to D abstraction.

Table II. Initial Rates for Some Reactions in C$_6$D$_6$ at 28 °C

reagents[a]	reactant or product monitored[b]	rate, M s^{-1}
n-Bu$_3$SnH/Me$_3$CCOCl[c]	n-Bu$_3$SnH	-6.0×10^{-5}
	Me$_3$CCHO	6.0×10^{-5}
n-Bu$_3$SnH/Me$_3$CCOCl/ Me$_3$CONNOCMe$_3$[d]	n-Bu$_3$SnH	-17.0×10^{-5}
	Me$_3$CCHO	6.0×10^{-5}
n-Bu$_3$SnH/Me$_3$CCOCl/ n-Bu$_3$SnCl	n-Bu$_3$SnH	-7.2×10^{-5}
	Me$_3$CCHO	7.2×10^{-5}
n-Bu$_3$SnH/Me$_3$CCHO/ n-Bu$_3$SnCl	n-Bu$_3$SnOCH_2-CMe$_3$	$\sim 1 \times 10^{-7}$
Me$_3$CCOCl/Me$_3$CCHO/ n-Bu$_3$SnCl	Me$_3$CCHO	-1.2×10^{-6}
	Me$_3$CC(O)-OCHClCMe$_3$	1.3×10^{-6}
Me$_3$CCOCl/n-Bu$_3$SnOCH$_2$CMe$_3$/ n-Bu$_3$SnCl	n-Bu$_3$SnOCH_2-CMe$_3$	-10.0×10^{-6}
	Me$_3$CC(O)-OCH_2CMe$_3$	9.8×10^{-6}

[a] Concentration of each reagent was 0.6 M unless otherwise noted. [b] Changes in reactant or product concentrations were monitored by ^{1}H NMR and using the signal of the italicized proton. [c] In a separate set of experiments a repeat measurement gave a rate of 5.7×10^{-5} and rates of 5.7×10^{-5}, 5.8×10^{-5}, and 5.6×10^{-5} M s^{-1} in the presence of 0.06 M galvinoxyl, duroquinone, and 2,2,6,6-tetramethylpiperidine-N-oxyl, respectively. [d] 0.1 M.

Stoichiometric Reaction of n-Bu$_3$SnH and Pivaloyl Chloride in Hydrocarbon Solvents. Aldehyde Formation. The major product formed in the spontaneous reaction of 0.6 M n-Bu$_3$SnH with 0.6 M Me$_3$CCOCl in n-octane is pivalaldehyde (see Table I). Pivalaldehyde is also the major product when the reaction is carried out in the presence of galvinoxyl, a commonly used inhibitor of free-radical processes.[23] However, initiation of this reaction with free radicals produced by the thermal decomposition of *tert*-butyl hyponitrite[28] or azocumene[29] causes isobutane to become the major product (Table I). This dramatic change in the products when the system is provided with a source of free radicals rules out any appreciable involvement of acyl radicals in the spontaneous reaction.

Further evidence against the intermediacy of free radicals in the spontaneous n-Bu$_3$SnH/Me$_3$CCOCl reaction was obtained by monitoring by NMR the kinetics of the reaction of 0.6 M n-Bu$_3$SnH with 0.6 M Me$_3$CCOCl in C$_6$D$_6$ at 28 °C. The rate of the spontaneous reaction, which was monitored both by the decrease in [n-Bu$_3$SnH] and by the increase in [Me$_3$CCHO], was 6.0×10^{-5} M s^{-1} (see Table II).[30] This rate was unaffected by the addition of 0.06 M quantities of three potential radical chain inhibitors: galvinoxyl,[23] duroquinone, and 2,2,6,6-tetramethylpiperidine-N-oxyl.[31] The addition of 0.1 M Me$_3$CONNOCMe$_3$

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(which would generate *tert*-butoxyl radicals at a rate of ca. 3×10^{-7} M s^{-1})[28] did not change the rate of pivalaldehyde formation, but it increased the rate of n-Bu_3SnH consumption to 17×10^{-5} M s^{-1} (Table II).[30] Clearly, the deliberate introduction of free radicals into the reaction mixture initiates a radical chain reaction which proceeds in parallel to the "normal" spontaneous reaction, consuming reagents but producing isobutane rather than pivalaldehyde. The spontaneous reaction cannot therefore be a radical chain process.

In contrast to the effect of free-radical initiators on the 0.6 M n-Bu_3SnH/0.6 M Me_3CCOCl reaction, the addition of an equimolar (0.6 M) quantity of n-Bu_3SnCl caused a slight accelerating effect on the "spontaneous" reaction (see Table II). This reaction product is not expected to have any effect on a radical chain reaction, but since it is probably a weak Lewis acid,[10] it might be expected to function as a catalyst for certain heterolytic reactions. It should be noted that the addition of n-Bu_3SnCl did not change the fundamental nature of the products.

The additional rate data given in Table II (for substrates at 0.6 M concentrations) relate to some of the individual reactions that, we believe, determine the composition of the final products of n-Bu_3SnH/Me_3CCOCl reactions. In the presence of n-Bu_3SnCl (the naturally produced Lewis acid catalyst) the formation of the tin alkoxide in the n-Bu_3SnH/Me_3CCHO reaction is very slow ($\sim 10^{-7}$ M s^{-1}). However, the tin alkoxide does undergo a relatively rapid ($\sim 10^{-5}$ M s^{-1}) stoichiometric reaction with Me_3CCOCl to form neopentyl pivalate.

$$n\text{-}Bu_3SnOCH_2CMe_3 + Me_3CCOCl \rightarrow n\text{-}Bu_3SnCl + Me_3CC(O)OCH_2CMe_3 \quad (8)$$

The reaction of aliphatic acid chlorides with aldehydes in the presence of Lewis acids is known to yield the corresponding α'-chloro ester.[32] The n-Bu_3SnCl-catalyzed Me_3CCOCl/Me_3CCHO reaction is relatively slow ($\sim 1.2 \times 10^{-6}$ M s^{-1}) but is sufficiently rapid to account for the formation of $Me_3CC(O)OCHClCMe_3$, a compound which can become a significant product under nonstoichiometric conditions (vide infra). It should be added that with some acid chlorides our rate measurements were not completely reproducible which leads us to believe that catalysts other than n-Bu_3SnCl may sometimes be inadvertently incorporated into n-$Bu_3SnH/RCOCl$ reaction mixtures.

Stoichiometric Reaction of n-Bu_3SnH and Pivaloyl Chloride without Solvent. Ester Formation. Walsh and Kuivila suggested[10] that esters were formed in the tin hydride/acid chloride reaction via the free-radical-chain sequence of reactions 2, 4, and 5. Our own results with 0.6 M n-Bu_3SnH and 0.6 M Me_3CCOCl show that although traces of ester are formed in the spontaneous reaction, more is certainly not produced in the radical-initiated reaction (see Table I). Furthermore, esters are not produced when *tert*-butoxyl radicals are generated in aliphatic aldehydes at 120 °C.[33] Even at lower temperatures (30 and 60 °C) we have found that absolutely no $Me_3CC(O)OCH_2CMe_3$ was formed when 0.2 M $Me_3CONNOCMe_3$ was completely decomposed in 7.4 M Me_3CCHO in benzene.[13] A radical mechanism for ester formation therefore appeared improbable.

In order to investigate the mechanism of ester formation we took advantage of the observation[9] that ester yields are higher for reactions involving neat tin hydride and acid chloride. The progress of the reaction between equimolar n-Bu_3SnH and Me_3CCOCl without added solvent was monitoried at 25 °C by NMR and by gas chromatography. Reactant and product concentrations during the first 6 h and after 156 h are shown in Figure 1. Within the first hour or so virtually all the tin hydride is consumed together with some 80% of the pivaloyl chloride, the major product(s) being pivalaldehyde (and the tin chloride). (Neopentyloxy)tributyltin, n-$Bu_3SnOCH_2CMe_3$, was also formed in appreciable yield together with a small amount of neopentanol. In addition, an even smaller quantity (ca. 0.01 M) of the 1:2 adduct of n-Bu_3SnH and Me_3CCHO, i.e., n-$Bu_3SnOCH(CMe_3)OCH_2CMe_3$, was formed, presumably[34,35] by a nonradical reaction between (neopentyloxy)tributyltin and pivalaldehyde.

$$n\text{-}Bu_3SnOCH_2CMe_3 + Me_3CCHO \rightarrow n\text{-}Bu_3SnOCH(CMe_3)OCH_2CMe_3 \quad (9)$$

The overall reaction continues slowly for at least the next 150 h with the pivaloyl chloride, (neopentyloxy)tributyltin, and a portion of the pivalaldehyde being converted to two new products: neopentyl pivalate, $Me_3CC(O)OCH_2CMe_3$, and the chloro ester $Me_3CC(O)OCHClCMe_3$. There is, however, no significant change in the amount of neopentyl alcohol. Figure 2 shows parts

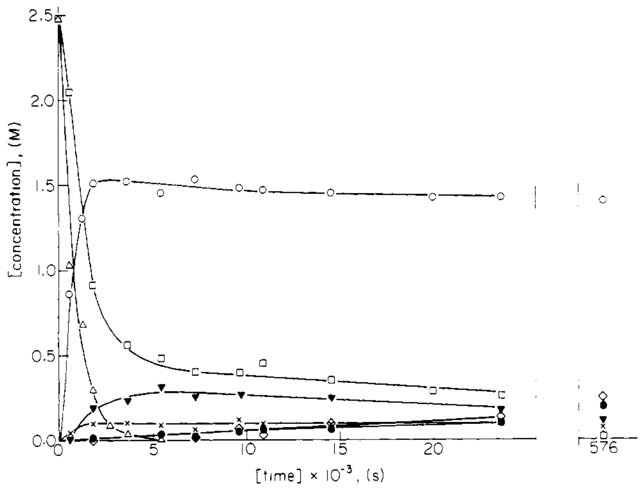

Figure 1. Stoichiometric reaction of n-Bu_3SnH and pivaloyl chloride without solvent at 25 °C: △, n-Bu_3SnH; □, Me_3CCOCl; ○, Me_3CCHO; ▼, n-$Bu_3SnOCH_2CMe_3$; ×, Me_3CCH_2OH; ◇, $Me_3CC(O)OCH_2CMe_3$; ●, $Me_3CC(O)OCHClCMe_3$.

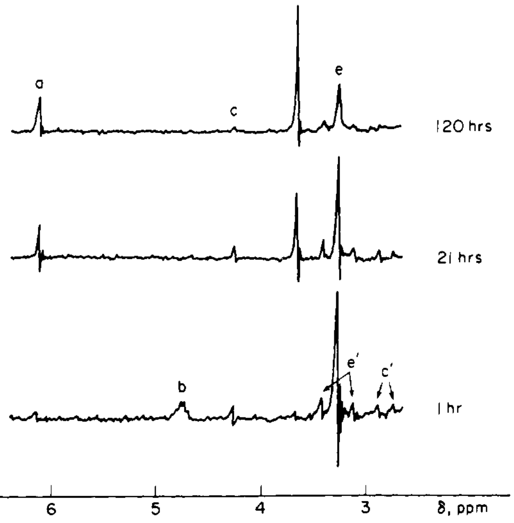

Figure 2. NMR spectra of the stoichiometric reaction of n-Bu_3SnH and pivaloyl chloride without solvent at 25 °C: (a) $Me_3CC(O)OCHClCMe_3$; (b) n-Bu_3SnH; (c) n-$Bu_3SnOCH(CMe_3)OCH_2CMe_3$; (c'), n-$Bu_3SnOCH(CMe_3)OCH_2CMe_3$ (doublet due to one of these protons, doublet due to another covered by e and e'); (d), $Me_3CC(O)OCH_2CMe_3$; (e) n-$Bu_3SnOCH_2CMe_3$; (e'), n-$Bu_3SnOCH_2CMe_3$, tin satelites (see also c').

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(31) Like galvinoxyl, this aminoxyl radical was shown by EPR spectroscopy to react quite rapidly with n-Bu_3SnH (see also ref 19) and so its inhibiting abilities in this system are questionable. The product(s) of the direct reaction of this aminoxyl and n-Bu_3SnH when treated with pivaloyl chloride yielded the corresponding acyloxy adduct to 2,2,6,6-tetramethylpiperidine-N-oxyl (see Experimental Section).

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Table III. Major Products Formed in Spontaneous Nonstoichiometric n-Bu_3SnH/Me_3CCOCl Reactions at 28 °C in the Absence of Solvent[a]

10^3 time, s	[n-$Bu_3Sn\mathit{H}$], M	[Me_3CCOCl], M	[$Me_3CC\mathit{H}O$], M	[$Me_3CC(O)OC\mathit{H}_2CMe_3$], M	[n-$Bu_3SnOC\mathit{H}_2CMe_3$], M	[$Me_3CC(O)OC\mathit{H}ClCMe_3$], M
0	2.95	1.48				
1.2	1.95	*b*	0.50	*c*	*c*	*c*
2.7	1.30	*b*	1.10	*c*	0.05	*c*
3.6	0.95	*b*	0.95	*c*	0.30[d]	*c*
6.0	0.70	*b*	0.70	*c*	0.55[d]	*c*
61.0	0.12	*b*	0.12	0.01	1.20[d]	*c*
430.0	0.01	*b*	*c*	0.01	1.30[d]	*c*
0	1.28	5.12				
1.2	0.02	*b*	1.13	*c*	*c*	*c*
6.0	*c*	*b*	1.00	0.01	*c*	0.02
61.0	*c*	*b*	0.53	0.01	*c*	0.41
160.0	*c*	*b*	0.24	0.01	*c*	0.75
430.0	*c*	*b*	*c*	0.01	*c*	1.05

[a] Loss of n-Bu_3SnH and formation of products monitored by ^1H NMR and using the signal of the italicized proton. [b] Not determined. [c] Not detected, concentration <0.01 M. [d] n-$Bu_3SnOC\mathit{H}(CMe_3)OCH_2CMe_3$ was also present at a concentration of ca. 0.02 M.

Table IV. Major Products of the Reaction of 0.6 M n-Bu_3SnH with 0.6 M 5-Hexenoyl Chloride in Benzene at 35 °C[a]

initiator (concn, M)	[hexenal], M	[2-methylcyclopentanone], M	[cyclohexanone], M	[$C_5H_9C(O)OC_6H_{11}$], M
none				0.218
none			0.002	0.199
none	0.045		0.008	0.235
$Me_3CONNOCMe_3$ (0.075)	0.035	0.111	0.055	0.178
$Me_3CONNOCMe_3$ (0.075)	0.086	0.111	0.028	0.079
$Me_3CONNOCMe_3$ (0.075)	0.008	0.047	0.055	0.107

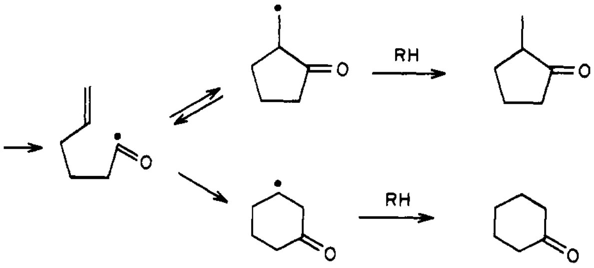
[a] Products analyzed by GC after 65 h. Note, these samples were deoxygenated by bubbling with argon, which may account for their poor reproducibility. (All other kinetic and product data were obtained on samples prepared by high-vacuum techniques.)

of some of the ^1H NMR spectra recorded during the reaction.

Nonstoichiometric Reaction of *n*-Bu_3SnH and Pivaloyl Chloride without Solvent. Further insights into the nature of the secondary reactions which yield products other than pivalaldehyde were obtained by NMR monitoring of nonstoichiometric spontaneous reactions between n-Bu_3SnH and Me_3CCOCl. Using a 2:1 mole ratio of n-Bu_3SnH/Me_3CCOCl in the absence of solvent yields pivalaldehyde as the major product in an approximately stoichiometric initial fast reaction. This compound is subsequently consumed in a slower reaction together with the remaining tin hydride. The final reaction product is (neopentyloxy)tributyltin (see Table III).

A 1:4 mole ratio of n-Bu_3SnH/Me_3CCOCl in the absence of solvent again yields pivalaldehyde as the major product of an approximately stoichiometric initial fast reaction. This is then converted, of necessity with the consumption of an equal quantity of pivaloyl chloride, into the chloro ester (see Table III).

Stoichiometric Reaction of *n*-Bu_3SnH and 5-Hexenoyl Chloride. Although our results with the n-Bu_3SnH/Me_3CCOCl system prove that pivalaldehyde and neopentyl pivalate are formed in the spontaneous reaction by nonradical mechanisms, this does not rule out a radical chain process for aldehyde and/or ester formation from other acid chlorides. Since we could see no reason why aldehyde should be formed by a radical chain *unless* radicals were deliberately introduced into the reactant mixture, we decided to concentrate on primary acid chlorides. These compounds are known to be less reactive toward n-Bu_3SnH and to yield considerably more of the ester product in their spontaneous reaction.[9] Since the acyl radicals derived from n-alkyl acid chlorides are known to have low rates for decarbonylation, we chose as our mechanistic probe 5-hexenoyl chloride. The corresponding acyl radical, like so many other radicals having this general type of structure,[36,37] undergoes cyclization to yield, eventually, two ketones, cyclohexanone and 2-methylcyclopentanone.[38,39] The former is the thermodynamically favored product, and the latter is the kinetically favored product.[28] However, the intermediate cyclopentanone-2-carbinyl radical can revert under normal experimental conditions to the starting 5-hexenoyl radical (a fact which has generally been overlooked).[40] The overall process can therefore be represented by reaction 10.



(10)

The formation of cyclic ketonic products from 5-hexenoyl chloride is, therefore, strong presumptive evidence that 5-hexenoyl radicals were involved as reactive intermediates. However, the relative yields of 2-methylcyclopentanone and cyclohexanone merely reflect the actual conditions of the experiment (concentration of alkyl radical trapping agent, temperature, etc.). Both of these cyclic ketones have been observed[40] in the free-radical-initiated reaction of n-Bu_3SnH with 5-hexenoyl chloride at temperatures somewhat above ambient. These earlier results are, of course, mechanistically irrelevant as far as the spontaneous reaction is concerned.

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(36) Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, Essay 4.

(37) (a) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073–3100. (b) Surzur, J. M. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum: New York, 1982; Vol. 2, pp 121–295.

(38) (a) Julia, M.; Maumy, M.; Mion, L. *Bull. Soc. Chim. Fr.* **1967**, 2641–2642. (b) Julia, M.; Maumy, M., *Ibid.* **1969**, 2415–2427. (c) *Ibid.* **1969**, 2427–2434.

(39) For some other examples of acyl radical cyclizations see: Montheard, J. P. *C. R. Hebd. Seances Acad. Sci.* **1965**, *260*, 577–580; Chatzopoulos, M.; Montheard, J. P. *Rev. Roum. Chim.* **1981**, *26*, 275–282.

(40) Cekovic, Z. *Tetrahedron Lett.* **1972**, 749–752. Walsh, E. J., Jr.; Messinger, J. M., II; Grudoski, D. A.; Allchin, C. A. *Ibid.* **1980**, *21*, 4409–4412. Cekovic, Z.; Cvetkovic, M.; Dokic, G. *Glas. Hem. Drus. Beograd* **1981**, *46*, 238–246.

Table V. Major Products Formed in the Spontaneous Reaction of 2.8 M n-Bu$_3$SnH with 1.4 M Hexanoyl Chloride in the Absence of Solvent at 28 °C[a]

10^3 time, s	$[n\text{-Bu}_3\text{Sn}H]$, M	$[\text{C}_4\text{H}_9\text{C}H_2\text{COCl}]$, M	$[\text{C}_5\text{H}_{11}\text{C}H\text{O}]$, M	$[\text{C}_5\text{H}_{11}\text{C(O)OC}H_2\text{C}_5\text{H}_{11}]$, M	$[n\text{-Bu}_3\text{SnOC}H_2\text{C}_5\text{H}_{11}]$, M
0	2.80	1.40			
2.5	2.50	1.10	0.3	0.0	0.0
9.0	1.70	0.20	0.6	0.2	0.0
52.2	1.0	0.0	0.0	0.4	0.4

[a] Changes in reactant and product concentrations were monitored by ^{1}H NMR and using the signal of the italicized proton.

The main products of the spontaneous and of the free-radical-initiated reaction of 0.6 M n-Bu$_3$SnH with 0.6 M 5-hexenoyl chloride in benzene at 35 °C show that the spontaneous process does not involve free radicals (see Table IV). Thus, the spontaneous reaction yields mainly the ester $\text{CH}_2\text{=CH(CH}_2)_3\text{C(O)O(CH}_2)_4\text{CH=CH}_2$, together with smaller quantities of 5-hexenal and cyclohexanone. No 2-methylcyclopentanone was detected in the spontaneous reaction. However, this compound was an important product of the reaction initiated with 0.075 M Me$_3$CONNOCMe$_3$. In fact, there was (generally) more 2-methylcyclopentanone than cyclohexanone in the initiated reactions.[41] This suggests that the small quantity of cyclohexanone formed in the spontaneous reaction may have been produced by a route that did not involve the 5-hexenoyl radical.

Stoichiometric Reaction of n-Bu$_3$SnH and Hexanoyl Chloride. This spontaneous reaction was chosen for a kinetic investigation involving a primary alkanoyl chloride because it could be monitored by NMR more easily than the n-Bu$_3$SnH/5-hexenoyl chloride reaction.

The reaction of equimolar n-Bu$_3$SnH and n-hexanoyl chloride in the absence of solvent was monitored at 28 °C. The decay of the reactants and the growth of the hexanal and hexyl hexanoate products are shown in Figure 3. The reaction rate is about 20–25% of that of the analogous n-Bu$_3$SnH/Me$_3$CCOCl reaction (cf. Figure 1). In contrast to the pivaloyl chloride reaction, no tributyltin alkoxide was detected under these conditions—though it is certainly formed (vide infra). It should be noted that the aldehyde concentration passes through a maximum shortly before the tin hydride and acid chloride have been consumed. In fact, the magnitude of the decrease in the aldehyde concentration, after its maximum, is approximately equal to the quantity of tin hydride and acid chloride remaining at this time and is also approximately equal to the quantity of ester formed at the end of the reaction, i.e.

$$\text{C}_5\text{H}_{11}\text{CHO} + n\text{-Bu}_3\text{SnH} + \text{C}_5\text{H}_{11}\text{COCl} \rightarrow \text{C}_5\text{H}_{11}\text{C(O)OC}_6\text{H}_{13} + n\text{-Bu}_3\text{SnCl} \quad (11)$$

The initial rate for the 0.6 M n-Bu$_3$SnH/0.6 M hexanoyl chloride reaction in C$_6$D$_6$ at 28 °C was 8.3×10^{-6} M s^{-1}, i.e., about 14% of the rate of the comparable pivaloyl chloride reaction. Evidence that this spontaneous reaction is also nonradical is provided by the observation that it can be catalyzed by n-Bu$_3$SnCl. The extent of the catalysis is even greater than that found for the spontaneous n-Bu$_3$SnH/pivaloyl chloride reaction. For example, the initial rate for the reaction catalyzed by equimolar (0.6 M) n-Bu$_3$SnCl was 4.0×10^{-5} M s^{-1}, a rate enhancement of nearly a factor of 5. As noted previously, n-Bu$_3$SnCl is not expected to have any effect on a radical chain reaction but, being a weak Lewis acid, it could function as a catalyst for certain heterolytic reactions.

Nonstoichiometric Reaction of n-Bu$_3$SnH and Hexanoyl Chloride. Ester Formation. Reaction 11 presumably occurs in two steps. By analogy with the pivaloyl chloride system it seemed likely that the first step involved a reaction of the aldehyde with tin hydride to form (hexyloxy)tributyltin, viz.

$$\text{C}_5\text{H}_{11}\text{CHO} + n\text{-Bu}_3\text{SnH} \rightarrow n\text{-Bu}_3\text{SnOC}_6\text{H}_{13} \quad (12)$$

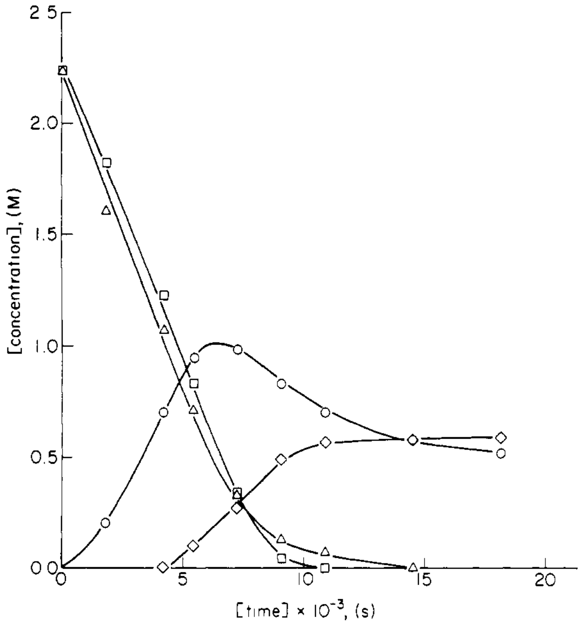

Figure 3. Stoichiometric reaction of n-Bu$_3$SnH and hexanoyl chloride without solvent at 28 °C: △, n-Bu$_3$SnH; □, hexanoyl chloride; ○, hexanal; ◇, hexyl hexanoate.

and the second step a reaction of the tin alkoxide with the acid chloride, viz.

$$n\text{-Bu}_3\text{SnOC}_6\text{H}_{13} + \text{C}_5\text{H}_{11}\text{COCl} \rightarrow \text{C}_5\text{H}_{11}\text{C(O)OC}_6\text{H}_{13} + n\text{-Bu}_3\text{SnCl} \quad (13)$$

In order to show that reaction 12 can occur under typical conditions, the reaction of n-Bu$_3$SnH with hexanoyl chloride at a 2:1 mole ratio in the absence of solvent was monitored by NMR at 28 °C. In the later stages of this reaction the hexanal which had been formed initially was completely consumed. It yields some additional ester (in an amount approximately equal to the amount of acid chloride remaining) but mainly the tin alkoxide (see Table V). The addition of sufficient hexanoyl chloride to this final reaction mixture again results in a rapid, exothermic reaction in which the tin alkoxide is converted to hexylhexanoate (reaction 13).

It is clear that aldehyde formation in the n-Bu$_3$SnH/n-alkyl acid chloride reaction is sufficiently slow that tin alkoxide formation via the n-Bu$_3$SnH/aldehyde reaction becomes important before the acid chloride has been completely consumed. However, the tin alkoxide does not accumulate until all the acid chloride had disappeared because these two compounds react rapidly to produce the ester.

Relative Reactivities of Some Aldehydes under Typical Conditions. The variation in the products formed from different acid chlorides could be due, in part, to differences in the reactivities of the aldehyde product. To explore this possibility pairs of aldehydes were added in twofold molar excess (1.2 M in each aldehyde) to a system consisting of 0.6 M n-Bu$_3$SnH/0.6 M hexanoyl chloride in n-octane containing a small quantity of *tert*-butylbenzene as an internal standard. The spontaneous reaction was allowed to proceed (in a sealed tube under vacuum, as usual) until all the n-Bu$_3$SnH and acid chloride had been consumed (ca. 15 h). The reaction mixture was then analyzed

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[41] As other have noted,[11] reproducibility for the initiated reaction was relatively poor. This may explain the disagreement in the literature[40] regarding the relative yields of 2-methylcyclopentanone and cyclohexanone. The reason(s) for our lack of reproducibility was (were) not explored since it did not disguise the major difference between the products of the initiated and spontaneous reactions.

Table VI. Relative Reactivities of Some Aldehydes in the Spontaneous Reaction between 0.6 M n-Bu_3SnH and 0.6 M Hexanoyl Chloride at 28 °C[a]

	relative reactivity from	
aldehyde	aldehyde consumption	ester formation
MeCHO	1.5	0.4
EtCHO	1.1	0.8
Me_2CHCHO	(1.0)[b]	(1.0)[b]
Me_3CCHO	0.7	0.7

[a] Two aldehydes present at 1.2 M each, solvent was n-octane, and analysis was by GC. [b] Assumed.

by GC for aldehydes remaining and esters formed. In all the experiments the amount of aldehyde consumed was larger than the amount of ester produced, for which reason relative reactivities were calculated, via the Ingold–Shaw equation,[42] both from aldehyde consumption and from ester formation (see Table VI). Analyses by NMR during the course of these reactions showed that products other than ester were formed in amounts which increased along the series $Me_3CCHO \approx Me_2CHCHO < EtCHO < MeCHO$. These products were identified as those arising from the additions of alkoxytributyltins to the aldehydes.[34,35] The consumption of aldehyde by this process is presumably responsible for the somewhat different relative reactivities calculated by aldehyde consumption and by ester formation. Despite this problem, it is quite clear that the aldehydes examined have rather similar reactivities toward the reagents present in the spontaneous tin hydride/hexanoyl chloride reaction.

Reactivities of Some Acid Chlorides. The rates of n-Bu_3SnH consumption were monitored by NMR in the spontaneous reactions of 0.6 M n-Bu_3SnH with 0.6 M acid chlorides in C_6D_6. Some problems of reproducibility were encountered with certain acid chlorides, but it was clear that reactivity decreased along the series $Me_3CCOCl > Me_2CHCOCl > EtCOCl \geqslant C_5H_{11}COCl > MeCOCl > c$-$C_3H_5COCl$ with the following approximate relative rates: 1.0:0.33:0.15:0.13:0.07:0.018.

Other Experiments. During the earlier stages of the present work it was by no means clear that free radicals were not involved in the spontaneous n-$Bu_3SnH/RCOCl$ reaction. Some of the "radical-oriented" experiments carried out at that time are of sufficient interest to be worth reporting.

(1) Attempt to Measure k_3 by Laser Flash Photolysis. Although our results with pivaloyl chloride prove that k_3 is not exceptionally large, an attempt was made to determine its magnitude by the technique of laser flash photolysis. The acetyl radical, which undergoes relatively slow decarbonylation,[43] was generated at room temperature in the presence of n-Bu_3SnH from 1,1-diphenylacetone by using the pulse from a Xe/HCl excimer laser (308 nm, ~5 ns, up to 80 mJ).

$$(C_6H_5)_2CHCOCH_3 \xrightarrow{h\nu} (C_6H_5)_2\dot{C}H + CH_3\dot{C}{=}O \quad (14)$$

This particular ketone was chosen as the acetyl radical precursor in order to minimize kinetic ambiguities which would arise from an attack on the tin hydride by the simultaneously produced alkyl radical. That is, the diphenylmethyl radical must be less reactive than the benzyl radical, and the room temperature rate constant for the n-$Bu_3SnH/C_6H_5\dot{C}H_2$ reaction has been shown[20] to be $\leqslant 3 \times 10^5\ M^{-1}\ s^{-1}$. After the laser pulse there was a slow growth of the absorption at 390 nm, which corresponds to an absorption maximum in the spectrum of the n-$Bu_3Sn\cdot$ radical.[44] However, our results allow us only to say that the rate constant for hydrogen abstraction from n-Bu_3SnH by $(C_6H_5)_2\dot{C}H$ and $CH_3\dot{C}{=}O$ is $\leqslant 2 \times 10^5\ M^{-1}\ s^{-1}$ at room temperature. Therefore, k_3 is at least an order of magnitude slower than the abstraction by nonresonance-stabilized alkyl radicals.

(2) EPR Spectroscopic Studies. If radicals were involved in n-$Bu_3SnH/RCOCl$ reactions then one might expect to observe them by EPR spectroscopy simply by the UV photolysis of hexa-n-butylditin in the presence of an acid chloride. A chlorine atom abstraction (reaction 2) would yield an acyl radical, viz.

$$(n\text{-}Bu_3Sn)_2 \xrightarrow{h\nu} 2(n\text{-}Bu_3Sn\cdot) \quad (15)$$

$$n\text{-}Bu_3Sn\cdot + RCOCl \rightarrow n\text{-}Bu_3SnCl + R\dot{C}{=}O \quad (2)$$

We also gave serious consideration at one time to an addition reaction, viz.[45]

$$n\text{-}Bu_3Sn\cdot + RCOCl \rightarrow n\text{-}Bu_3SnO\dot{C}(Cl)R \quad (16)$$

If this addition was followed by reaction with the tin hydride and then an elimination of n-Bu_3SnCl, i.e.

$$n\text{-}Bu_3SnH + n\text{-}Bu_3SnO\dot{C}(Cl)R \rightarrow n\text{-}Bu_3Sn\cdot + n\text{-}Bu_3SnOCH(Cl)R \quad (17)$$

$$n\text{-}Bu_3SnOCH(Cl)R \rightarrow n\text{-}Bu_3SnCl + RCHO \quad (18)$$

then an alternative radical-chain route to aldehyde would exist which would not involve acyl radicals. This mechanism would provide a potential explanation for the virtual absence of carbon monoxide from the reaction products which had been reported by Kuivila and Walsh.[9]

Experiments were carried out which involved the direct photolysis in the cavity of an EPR spectrometer of deoxygenated hydrocarbon solutions of hexa-n-butylditin or hexamethylditin and a number of acid chlorides at low and at ambient temperatures.[46,47] Most of the acid chlorides examined including in particular c-C_3H_5COCl,[49,50] $CH_3(CH_2)_5COCl$,[51,52] and Me_3CCH_2COCl[52] were chosen because the corresponding acyl radicals should have been easy to detect and identify, since they had been generated previously by H-atom abstraction from the corresponding aldehyde and been shown to have relatively sharp EPR spectral lines.[49,52] Although EPR signals were obtained with most of the acid chlorides, the corresponding acyl radicals were not detected under any conditions.[53] Furthermore, the observed spectra were generally due to mixtures of radicals, some of which were relatively persistent, and so we are unable to say whether any n-$Bu_3SnO\dot{C}(Cl)R$ radicals were formed. We are inclined to attribute our failure to observe any acyl radicals to the buildup of the persistent radicals. Photolysis in a flow system, which might have overcome these problems, was not explored.

Finally, pivaloyl chloride gave the readily identified *tert*-butyl radical on photolysis with $(n$-$Bu_3Sn)_2$ and di-*tert*-butyl peroxide. Unfortunately, the *tert*-butyl radical was also formed on photolysis of pivaloyl chloride and the peroxide, so n-Bu_3Sn radicals are not required for its formation.

(3) Stoichiometric Reaction of n-Bu_3SnH and Cyclopropylcarbonyl Chloride. Relative to cyclopropylcarbinyl, the cyclo-

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(42) Ingold, C. K.; Shaw, F. R. *J. Chem. Soc.* **1927**, 2918–2926.

(43) For a summary of available kinetic data, see ref 17.

(44) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 5399–5400.

(45) For an analogous reaction scheme which accounts for the formation of 2-phenyltetrahydrofuran in the n-$Bu_3SnH/C_6H_5CO(CH_2)_2Cl$ reaction, see: Maillard, B.; Gardrat, C.; Bourgeois, M.-J. *J. Organomet. Chem.* **1982**, *236*, 61–68.

(46) We are indebted to Professor L. Lunazzi for carrying out many of these experiments.

(47) Di-*tert*-butyl peroxide was added, on occasion, to enhance the yield of trialkylstannyl radicals.[48]

(48) Watts, G. B.; Ingold, K. U. *J. Am. Chem. Soc.* **1972**, *94*, 491–494. Cooper, J.; Hudson, A.; Jackson, R. A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1056–1060.

(49) Blum, P. M.; Davies, A. G.; Sutcliffe, R. *J. Chem. Soc., Chem. Commun.* **1979**, 217–218.

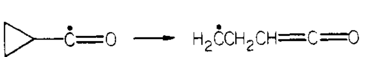
(50) Davies, A. G.; Sutcliffe, R. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1483–1488.

(51) Davies, A. G.; Sutcliffe, R. *J. Chem. Soc., Chem. Commun.* **1979**, 473–475.

(52) Davies, A. G.; Sutcliffe, R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 819–824.

(53) The only acyl radical to have been observed when $(n$-$Bu_3Sn)_2$ has been photolyzed in the presence of an acid chloride is 2,4,6-tri-*tert*-butylbenzoyl[52] which may well be persistent.

propylacyl radical is known to undergo a slow ring opening.[49,50]



(19)

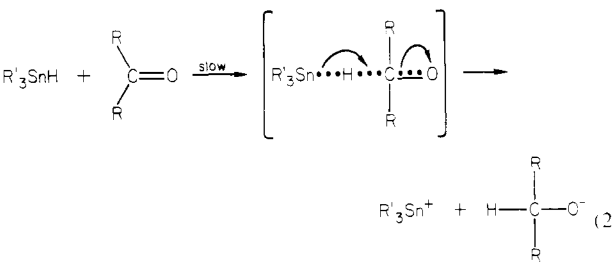
Nevertheless, it seemed possible that such a process might occur in the n-Bu_3SnH/c-C_3H_5COCl reaction if radicals were involved. For this reason a brief study of this reaction was undertaken by using 0.6 M reagents in C_6D_6 at 35 °C. The reaction was slow. After 48 h there remained 0.19 M n-Bu_3SnH and there had been formed 0.24 M c-C_3H_5CHO, 0.09 M c-$C_3H_5C(O)OCH_2$(c-C_3H_5), and 0.08 M c-$C_3H_5CH_2OSnBu_3$-n. There was no sign of any ring-opened products.[54]

Discussion

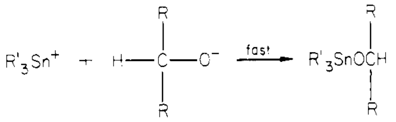
As a number of our experiments demonstrate, the spontaneous reaction between n-Bu_3SnH and acid chlorides does not involve free radicals. Specifically, the following results show that aldehyde is not formed via acyl radicals as intermediates.

In the n-Bu_3SnH/Me_3CCOCl reaction (i) $Me_3C\dot{C}{=}O$ decarbonylates much more rapidly than it reacts with n-Bu_3SnD, (ii) Me_3CCHO is a major product of the spontaneous reaction, but Me_3CH is formed in the radical-initiated process (see Table I), (iii) neither the product nor the reaction rate is affected by some typical inhibitors of radical-chain processes, (iv) the rate of formation of Me_3CCHO is unchanged by addition of a free-radical initiator, but the rate of consumption of n-Bu_3SnH is accelerated (see Table II), and (v) the reaction rate is slightly accelerated by the reaction product, n-Bu_3SnCl, presumably as a consequence of its weak Lewis acidity. In the n-Bu_3SnH/5-hexenoyl chloride reaction (vi) there is no 2-methylcyclopentanone and very little cyclohexanone formed in the spontaneous reaction, but both of these compounds are major products in the radical initiated process (see Table IV). Furthermore (vii) the n-Bu_3SnH/$Me\dot{C}{=}O$ reaction is relatively slow ($k < 2 \times 10^5$ M^{-1} s^{-1}). Similarly, the following results show that ester is not formed via acyl radicals as intermediates: (i) neopentyl pivalate was not formed when *tert*- butoxyl radicals were generated in Me_3CCHO, the major product being Me_3CH, (ii) the yield of ester in the n-Bu_3SnH/5-hexenoyl chloride reaction was decreased by the addition of a free-radical initiator, (iii) esters appear to be formed in the n-Bu_3SnH/pivaloyl chloride and in the n-Bu_3SnH/hexanoyl chloride reactions in two-step processes involving alkoxytributylins as intermediates.

It is well-known that not all reactions involving tin hydrides occur via free radicals.[4b,27,56-60] Of particular interest with respect to n-Bu_3SnH/RCOCl reactions are certain addition reactions involving tin hydrides. These particular reactions occur by a nonradical process, which is favored by electron-withdrawing substituents adjacent to the carbonyl group and is believed to involve a nucleophilic attack of the hydride hydrogen on carbon, viz.[60]

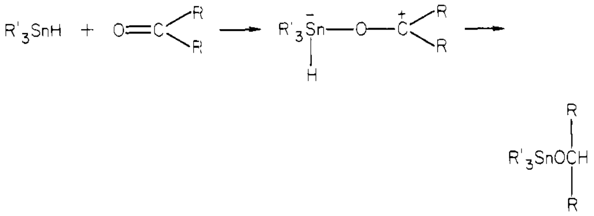


$$R'_3SnH + \overset{R}{\underset{R}{C}}{=}O \xrightarrow{slow} \left[R'_3Sn\cdots H\cdots\overset{R}{\underset{R}{C}}\cdots O\right] \longrightarrow R'_3Sn^+ + H-\overset{R}{\underset{R}{C}}-O^- \qquad (20)$$



$$R'_3Sn^+ + H-\overset{R}{\underset{R}{C}}-O^- \xrightarrow{fast} R'_3SnO\overset{R}{\underset{R}{C}}H \qquad (21)$$

Since acid chlorides certainly have an electron-withdrawing substituent attached to the carbonyl carbon, they might be expected to react with tin hydrides by a similar mechanism. However, the reactivity order found for the following acid chlorides makes this seem rather unlikely since the more bulky alkyl groups should retard, rather than accelerate, hydride attack at carbon: $Me_3CCOCl > Me_2CHCOCl > EtCOCl > MeCOCl$. An alternative mechanism that would be rather more consistent with the observed reactivity order would involve nucleophilic attack of oxygen on tin as suggested by Cullen and Styan,[57] with the formation of a 5-coordinated tin species as an intermediate, viz.



$$R'_3SnH + O{=}CR_2 \longrightarrow R'_3\overset{-}{\underset{H}{Sn}}-O-\overset{+}{C}R_2 \longrightarrow R'_3SnO\overset{R}{\underset{R}{C}}H \qquad (22)$$

The analogous (α-chloroalkoxy)tin species which would be formed from an acid chloride would be expected to be very unstable[61] and to decompose rapidly to aldehyde and tin chloride.

$$R'_3SnOCHRCl \rightarrow R'_3SnCl + RCHO \qquad (23)$$

The observed catalysis by n-Bu_3SnCl may be due to its effect on solvent polarity rather than to a specific activation via complex formation of the acid chloride or tin hydride. Of course, other possible mechanisms for aldehyde formation in the spontaneous n-Bu_3SnH/RCOCl reaction such as those involving four-center cyclic transition states leading directly to (α-chloroalkoxy)tributyltin or to aldehyde and n-Bu_3SnCl cannot be ruled out by our results. All we can, and do, rule out are radical processes. The most likely mechanism for ester formation is via an alkoxytin intermediate which then reacts with further acid chloride to yield the tin chloride and the ester (e.g., reactions 12 and 13). This mechanism was considered by Walsh and Kuivila,[10] who decided that while it undoubtedly provided some of the ester it could not be the major source of this compound. Their arguments were kinetic in nature but were based in part on their assumption that the n-Bu_3SnH/RCOCl reaction was a free-radical process. These workers showed that the n-Bu_3SnH/RCHO reaction could be catalyzed by n-Bu_3SnCl. However, their study of the n-Bu_3SnH/Me_2CHCHO reaction indicated that even the n-Bu_3SnCl-catalyzed process was too slow for there to be a major route to ester via the tin alkoxide. Our own kinetic data on the n-Bu_3SnCl-catalyzed n-Bu_3SnH/Me_3CCHO reaction (Table II, entry 4) serve to confirm Walsh and Kuivila's conclusion that this class of reactions is fairly slow under these conditions. However, some of our other results show that tributyltin alkoxide can become a significant product in n-Bu_3SnH/RCOCl reactions under other conditions (see, Table III, first reaction and Figures 1 and 2 for Me_3CCOCl), which suggests that catalysts that are more effective than n-Bu_3SnCl (e.g., possibly the acid chloride itself) may be present under normal experimental conditions. Furthermore, we have shown that n-$Bu_3SnOCH_2CMe_3$ reacts rapidly with Me_3CCOCl and that n-$Bu_3SnOC_6H_{13}$ reacts even more rapidly with $C_5H_{11}COCl$ to form the corresponding esters in both cases. We therefore presume that the major route to ester is via the tin

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(54) However, at 80 °C a radical-initiated reaction has yielded a trace of ring-opened products.[55] Thus, to 6.9 g of c-C_3H_5COCl containing azobisisobutyronitrile was added dropwise 19.2 g of n-Bu_3SnH. No reaction occurred until the mixture was heated to 80 °C at which point a violent reaction occurred, which gave on isolation 2.7 g of c-C_3H_5CHO, 1.35 g of c-$C_3H_5C(O)OCH_2$ (c-C_3H_5), 0.45 g of c-$C_3H_5C(O)OCH{=}CHCH_2CH_3$, and 21.5 g of residue.[55]

(55) Pereyre, M., private communication.

(56) Neumann, W. P.; Heymann, E. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 100.

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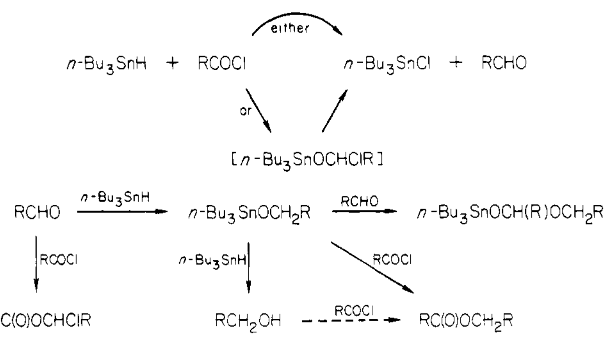
Scheme I



alkoxide/acid chloride reaction. The tin alkoxide is formed by the well-known,[62] nonradical reaction of tin hydride with aldehyde.[56,60,63]

There is also, of course, a second potential route to ester[64] involving the alcohol as an intermediate, the latter being formed by reaction of the tin alkoxide with tin hydride.[10,27,35,62,65]

$$\mathrm{Bu_3SnOCH_2R} + n\text{-}\mathrm{Bu_3SnH} \rightarrow (n\text{-}\mathrm{Bu_3Sn})_2 + \mathrm{RCH_2OH} \quad (24)$$

$$\mathrm{RCH_2OH} + \mathrm{RCOCl} \rightarrow \mathrm{RC(O)OCH_2R} + \mathrm{HCl} \quad (25)$$

This pathway to ester appears to be of minor importance under normal reaction conditions.

The $\mathrm{Bu_3SnH/RCOCl}$ reactions can, under certain conditions, yield other aldehyde-derived products. Thus, α'-chloro ester can become a significant product, being formed by reaction of the aldehyde with unreacted acid chloride.[32]

$$\mathrm{RCHO} + \mathrm{RCOCl} \rightarrow \mathrm{RC(O)OCHClR} \quad (26)$$

A minor product that has been identified only by NMR appears to be the 2:1 n-$\mathrm{Bu_3SnH/RCHO}$ adduct. Such products are to be expected since they are readily produced by the reaction of aldehyde with tin alkoxides.[34,35]

$$\mathrm{RCHO} + n\text{-}\mathrm{Bu_3SnOCH_2R} \rightarrow n\text{-}\mathrm{Bu_3SnOCH(R)OCH_2R} \quad (27)$$

All of our results can be accommodated by the nonradical reactions of Scheme I. Product yields are obviously going to depend on such factors as the initial stoichiometry of the tin hydride/acid chloride reagents, their concentration, and for fast reactions the order of addition. In particular, the aldehyde/ester ratio is going to depend on the relative reactivity of the acid chloride and the aldehyde derived from it toward the tin hydride remaining in the reaction mixture. However, now that the reaction mechanism is understood it should be quite possible to reduce acid chlorides to aldehydes in good yields with tin hydrides without the necessity for a palladium[66-69] catalyst. Of course, if a free-radical process is superposed on top of (i.e., in parallel with) the spontaneous reaction, the aldehyde yield might be further improved if decarbonylation of the acyl radical was slow. However, a detailed kinetic interpretation under such conditions would be mind boggling.

Experimental Section

Most reactants were commercially available or were readily prepared by standard procedures. These compounds were all purified by distillation or preparative gas chromatography (GC) and were kept under a nitrogen atmosphere before use. Their purity was checked by analytical GC. (Neopentyloxy)tri-n-butyltin was obtained by the known reaction of neopentyl alcohol and bis(tri-n-butyltin) oxide.[70] A Varian Vista 6000 chromatograph was used for the GC analyses, which were carried out on $^1/_8$-in.-i.d., 12-ft, 12% OV 101 Chromosorb W (HP) or 0.2-mm-i.d. 12-m, methylsilicone columns. An HP 5995 GC/MS spectrometer was also employed. NMR spectra were recorded on a Varian EM 360A spectrometer and EPR spectra on a Varian E104 spectrometer.

General Procedure. Unless otherwise stated, the samples were prepared volumetrically in a drybox, with the acyl chloride being added to a solution of n-Bu$_3$SnH or to neat n-Bu$_3$SnH. The prepared mixtures were immediately transferred into Pyrex or quartz ampules, degassed under vacuum, and sealed. The reactions were then monitored by NMR and/or GC and, in some cases, also by EPR spectroscopy.

The following NMR signals were used to monitor the progress of the reactions in the pivaloyl chloride/or n-hexanoyl chloride/tri-n-butyltin hydride systems (chemical shifts are given in δ): n-Bu$_3$SnH, 4.84 (sept), J(6 H) ~ 2 Hz; Me$_3$CCHO, 9.42 (s); n-Bu$_3$SnOCH_2CMe$_3$, 3.33 (s), J(Sn–H) = 18 Hz; Me$_3$CC(O)OCH_2CMe$_3$, 3.73, (s); Me$_3$CC(O)-OCHClCMe$_3$, 6.17, (s); n-Bu$_3$SnOCH(CMe$_3$)OCH$_2$CMe$_3$, 4.30, (s) J (Sn–H) = 26 Hz; C$_4$H$_9$CH_2COCl, 2.88 (t), J(2 H) = 7 Hz; C$_5$H$_{11}$CHO, 9.65 (t), J(2 H) = 1.5 Hz; C$_5$H$_{11}$C(O)OCH_2C$_5$H$_{11}$, 4.02 (t), J(2 H) = 6 Hz; n-Bu$_3$SnOCH_2C$_5$H$_{11}$, 3.70 (t), J(2 H) = 6 Hz.

The above chemical shifts are given for neat systems. Small changes were observed for some compounds between these values and those observed in solution. In the NMR experiments in C$_6$D$_6$ the concentrations of the components of the reaction mixtures were measured by using the residual proton signal which had been calibrated against cyclohexane. In reactions without solvent, benzene was used as the standard. The components of the reaction mixtures were identified by GC and by GC/MS analysis by comparison with authentic samples whenever possible.

Formation of Pivaloyl Radicals in the Presence of n-Bu$_3$SnD. A mixture of 53 μL (0.2 mM) of n-Bu$_3$SnD, 150 μL (1.4 mM) of Me$_3$CCHO, and 9 mg (0.05 mM) of Me$_3$CONNOCMe$_3$ was sealed under vacuum and heated to 50 °C for 16 h (ca. 8 half-lives of hyponitrite) and then cooled to −80 °C, opened, diluted with cold (−30 °C) toluene, and analyzed by GC/MS. The M/M + 1 ratio revealed the presence of ~16% of Me$_3$CD in the isobutane, but there was no detectable deuterium enrichment of the pivalaldehyde.

Stoichiometric Reactions of n-Bu$_3$SnH and Pivaloyl Chloride in n-Octane. Mixtures of 161 μL (0.6 mM) of n-Bu$_3$SnH, 74 μL (0.6 mM) of Me$_3$CCOCl, 760 μL of n-octane, and 5 μL of benzene were sealed under vacuum and kept at either 25 or 60 °C for several hours, cooled to −20 °C and opened, and their contents were analyzed by GC. Similar reactions were also carried out with the addition of either 25 mg (0.06 mM) of galvinoxyl, 1.7 mg (0.01 mM) of Me$_3$CONNOCMe$_3$, or 1.4 mg (0.01 mM) of azocumene.

Kinetic NMR Measurements for n-Bu$_3$SnH/Pivaloyl Chloride in C$_6$D$_6$. The following reaction mixtures were sealed under vacuum: (i) 765 μL of C$_6$D$_6$, 161 μL (0.6 Me$_3$CCOCl; of n-Bu$_3$SnH, 74 μL (0.6 mM) of Me$_3$CCOCl; (ii) 765 μL of C$_6$D$_6$, 17 mg (0.1 mM) of Me$_3$CONNOCMe$_3$, 161 μL (0.6 mM) of n-Bu$_3$SnH, 74 μL (0.6 mM) of Me$_3$CCOCl; (iii) 362.5 μL of C$_6$D$_6$, 5 mg (0.03 mM) of duroquinone, 80.5 μL (0.3 mM) of n-Bu$_3$SnH, 37 μL (0.3 mM) of Me$_3$CCOCl; (iv) 362.5 μL of C$_6$D$_6$, 12.5 mg (0.03 mM) of galvinoxyl, 80.5 μL (0.3 mM) of n-Bu$_3$SnH, 37 μL (0.3 mM) of Me$_3$CCOCl; (v) 362.5 μL of C$_6$D$_6$, 4.7 mg (0.03 mM) of 2,2,6,6-tetramethylpiperidine-N-oxyl, 80.5 μL (0.3 mM) of n-Bu$_3$SnH, 37 μL (0.3 mM) of Me$_3$CCOCl; (vi) 300.5 μL of C$_6$D$_6$, 82 μL (0.3 mM) of n-Bu$_3$SnCl, 80.5 μL (0.3 mM) of n-Bu$_3$SnH, 37 μL (0.3 mM) of Me$_3$CCOCl; (vii) 304.5 μL of C$_6$D$_6$, 82 μL (0.3 mM) of n-Bu$_3$SnCl, 80.5 μL (0.3 mM) of n-Bu$_3$SnH, 33 μL (0.3 mM) of Me$_3$CCHO; (viii) 348 μL of C$_6$D$_6$, 82 μL (0.3 mM) of n-Bu$_3$SnCl, 33 μL (0.3 mM) of Me$_3$CCHO, 37 μL (0.3 mM) of Me$_3$CCOCl; and (ix) 300 μL of C$_6$D$_6$, 82 μL (0.3 mM) of n-Bu$_3$SnCl, 81 μL (~0.3 mM) of n-Bu$_3$SnOCH$_2$CMe$_3$, 37 μL (0.3 mM) of Me$_3$CCOCl.

NMR spectra were recorded at appropriate time intervals (several minutes or a few hours, depending upon the rate of a particular reaction).

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(63) In n-Bu$_3$SnH/RCOCl reaction this particular process may be catalyzed by unidentified Lewis acids present initially or formed during the reaction.

(64) A referee has suggested a termolecular n-Bu$_3$SnH/RCOCl/RCHO reaction as yet a third possibility. Such a process can be ruled out for pivaloyl chloride since almost no ester is formed in the initial stages of the reaction during which tin hydride is still present and the reaction products are pivalaldehyde and tin alkoxide. In this system, ester is produced during the second slow part of the reaction in the absence of tin hydride and with a decrease in the concentrations of pivaloyl chloride and tin alkoxide. These two reactants are converted almost quantitatively to ester (see Figure 1). In contrast, a termolecular reaction cannot be explicitly ruled out for hexanoyl chloride since the tin alkoxide could not be detected in this reaction system. Nevertheless, we consider a termolecular route to ester to be unlikely since our failure to detect n-Bu$_3$SnOC$_6$H$_{13}$ can be readily accounted for by its rapid, exothermic reaction with C$_5$H$_{11}$COCl (see Results).

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The initial rates of reaction were obtained from the slopes of the plots of the concentration of a particular reactant or product vs. time.

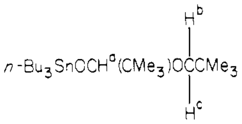
The concentrations of the products of reaction i after 7.5 h, as determined by NMR, were Me_3CCHO, 0.55 M; $Me_3CC(O)OCH_2CMe_3$, <0.01 M (not detected); and n-$Bu_3SnOCH_2CMe_3$, <0.01 M (not detected). The products from reaction vi after 6 h were Me_3CCHO, 0.47 M; $Me_3CC(O)OCH_2CMe_3$, 0.012 M; and n-$Bu_3SnOCH_2CMe_3$, 0.039 M. The reaction mixtures containing galvinoxyl (iv) and 2,2,6,6-tetramethylpiperidine-*N*-oxyl (v) were sealed in quartz tubes and monitored by both NMR and EPR. The EPR signals from both of these free radicals decayed rapidly. A rapid decay was also observed with *n*-octane or benzene solutions of *n*-Bu_3SnH (0.6 M) and galvinoxyl (0.06 M) or 2,2,6,6-tetramethylpiperidine-*N*-oxyl (0.06 M). A GC/MS analysis of the products of reaction v showed the formation of the pivaloyl adduct of 2,2,6,6-tetramethylpiperidine-*N*-oxyl: mass spectrum, *m/e* (relative intensity) 241 (1.7) M^+, 226 (12.4), 156 (2.9), 126 (27.3), 85 (8.0), 57 (100). The formation of this product does not mean that pivaloyl radicals were present during reaction v since the same adduct was found when pivaloyl chloride was added to the products of the *n*-Bu_3SnH/2,2,6,6-tetramethylpiperidine-*N*-oxyl reaction.

Free-Radical Decomposition Reaction of Pivaldehyde. Mixtures of 200 μL (1.8 mM) of Me_3CCHO, 8.7 mg (0.05 mM) of $Me_3CONNOCMe_3$, and 50 μL of benzene (standard) were sealed under vacuum and kept at 30 or 60 °C for 12 or 3 days, respectively, before being analyzed by GC. The aldehyde concentration decreased by about 2 M in both cases. The only product detected was isobutane.

Stoichiometric Reaction of *n*-Bu_3SnH with Pivaloyl Chloride without Solvent. A mixture of 1288 μL (4.8 mM) of *n*-Bu_3SnH, 590 μL (4.8 mM) of Me_3CCOCl, and 40 μL of benzene (standard) was prepared and transferred into a number of Pyrex tubes, which were then degassed and sealed under vacuum. The progress of the reaction was monitored by NMR and by GC. That is, after recording an NMR spectrum a particular sample was cooled to −20 °C and opened, and its contents were analyzed by GC. As an alternative procedure, a nitrogen-flushed sample was sealed with a septum and placed in an NMR tube. Spectra were recorded followed immediately by GC analyses of a small portion of the reaction mixture, which was withdrawn through the septum with a hypodermic syringe.

The concentration of *n*-$Bu_3Sn\mathit{H}$, $Me_3CC\mathit{H}O$, *n*-$Bu_3SnOC\mathit{H}_2CMe_3$, and *n*-$Bu_3SnOC\mathit{H}(CMe_3)OCH_2CMe_3$ were measured by means of NMR by using the integration of the signals of the indicated protons, while those of Me_3CCOCl, Me_3CCH_2OH, $Me_3CC(O)OCH_2CMe_3$, and $Me_3CC(O)OCHClCMe_3$ were determined by GC analysis.

The identification of one of the products as *n*-$Bu_3SnOCH(CMe_3)OCH_2CMe_3$ was supported by the comparison of the NMR spectrum of the above reaction mixture with that obtained during the reaction of *n*-$Bu_3SnOCH_2CMe_3$ with a fourfold excess of Me_3CCHO without solvent. The product of this reaction exhibited NMR signals which were assigned as follows:



$$n\text{-}Bu_3SnOCH^a(CMe_3)O\overset{\displaystyle H^b}{\underset{\displaystyle H^c}{C}}CMe_3$$

signal a, (s), 4.30, *J*(Sn–H) = 26 Hz; signal b, (d), 3.41, $J(H_b–H_c)$ = 8 Hz; signal c, (d), 2.86, $J(H_c–H_b)$ = 8 Hz

Nonstoichiometric Reactions of *n*-Bu_3SnH and Pivaloyl Chloride. The following reaction mixtures were sealed under vacuum as usual: (x) 161 μL (0.6 mM) of *n*-Bu_3SnH, 37 μL (0.3 mM) of Me_3CCOCl, 5 μL benzene (standard) and (xi) 40 μL (0.15 mM) of *n*-Bu_3SnH, 74 μL (0.6 mM) of Me_3CCOCl, 2.5 μL of benzene (standard). The progress of the reactions and composition of the reaction mixtures were followed by NMR.

Stoichiometric Reactions of *n*-Bu_3SnH and 5-Hexenoyl Chloride. Mixtures of 41.5 μL (0.3 mM) of hexenoyl chloride and 378 μL of benzene or of a 0.01 M solution of $Me_3CONNOCMe_3$ in benzene were degassed by bubbling with argon and then cooled in an ice bath, and 80.5 μL (0.3 mM) of *n*-Bu_3SnH was added. The mixtures were kept for 65 h at 35 °C and were then analyzed by GC on a Carbowax 20M 5%, Chromosorb W, 2-m column.

Stoichiometric Reaction of *n*-Bu_3SnH and Hexanoyl Chloride. The following reaction mixutres were prepared by the usual procedure: (xii) 161 μL (0.6 mM) of *n*-Bu_3SnH, 84 μL (0.6 mM) of C_5H_{11} COCl, 5 μL of benzene (standard); (xiii) 377.5 μL of C_6D_6, 80.5 μL (0.3 mM) of *n*-Bu_3SnH, 42 μL (0.3 mM) of $C_5H_{11}COCl$; and (xiv) 295.5 μL of C_6D_6, 80.5 μL (0.3 mM) of *n*-Bu_3SnH, 42 μL (0.3 mM) of $C_5H_{11}COCl$, 82 μL (0.3 mM) of *n*-Bu_3SnCl.

The reactions were monitored by NMR, using signals of the following protons: *n*-$Bu_3Sn\mathit{H}$, $C_5H_{11}C\mathit{H}O$, $C_4H_9C\mathit{H}_2COCl$, and $C_5H_{11}C(O)OC\mathit{H}_2C_5H_{11}$. The initial rates of the reactions were taken from the slopes of the plots of concentration of reactant or product vs. time.

The concentrations of the products of reaction xiii after 69 h were $C_5H_{11}CHO$, 0.48 M, and $C_5H_{11}C(O)OCH_2C_5H_{11}$, ~0.01 M, and those of reaction xiv after 24 h were $C_5H_{11}CHO$, 0.44 M, and $C_5H_{11}C(O)OCH_2C_5H_{11}$, 0.06 M.

Nonstoichiometric Reaction of *n*-Bu_3SnH and Hexanoyl Chloride. A reaction mixture consisting of 322 μL (1.2 mM) of *n*-Bu_3SnH, 84 μL (0.6 mM) of $C_5H_{11}COCl$, and 30 μL of benzene (standard) was prepared and the reaction was followed by NMR monitoring of signals due to the following protons: *n*-$Bu_3Sn\mathit{H}$, $C_5H_{11}C\mathit{H}O$, $C_5H_{11}C(O)OC\mathit{H}_2C_5H_{11}$, and *n*-$Bu_3SnOC\mathit{H}_2C_5H_{11}$. When the reaction was completed (all aldehyde and acid chloride consumed) the ampule was opened and 168 μL (1.2 mM) of $C_5H_{11}COCl$ was added. The NMR spectrum showed that the previously formed (hexyloxy)tri-*n*-butyltin had been converted into additional hexyl hexanoate essentially immediately.

Relative Reactivities of Some Aldehydes. Reaction mixtures were prepared containing 80.5 μL (0.3 mM) of *n*-Bu_3SnH, 42 μL (0.3 mM) of $C_5H_{11}COCl$, 10 μL of *tert*-butylbenzene (standard), 55 μL (0.6 mM) of Me_2CHCHO, 0.6 mM of another aldehyde, and an amount of *n*-octane just sufficient to increase the volume to 500 μL. Me_3CCHO, EtCHO, and MeCHO were used in these experiments. When the reaction was complete, i.e., when all the tin hydride had reacted (usually ca. 15 h as determined by NMR), the samples were cooled to −20 °C, diluted with cold (−20 °C) octane (to get better resolution on a GC capillary column), and analyzed. The quantities of esters formed and of aldehydes consumed were determined. Relative reactivities of the aldehydes were calculated by the Ingold–Shaw equation.[42]

The NMR spectra revealed the presence of additional products which were assumed to result from the addition of alkoxytri-*n*-butyltins to an aldehyde. The signals of the indicated proton *n*-$Bu_3SnOC\mathit{H}(R)OCH_2R'$ appeared in the region of δ 4.3–5.0 with coupling to the α protons (if any) of the R group of ca. 5–6 Hz.

Reactivities of Some Acid Chlorides. The samples were prepared as described for the reactions of *n*-hexenoyl chloride. Bu_3SnH (0.6 M) was allowed to react spontaneously with 0.6 M acid chloride in C_6D_6. The rates of decay of tin hydride in the reactions with Me_3CCOCl, $Me_2CHCOCl$, EtCOCl, MeCOCl, and c-C_3H_5COCl were taken as a measure of the reactivities of chlorides. These measurements were carried out by NMR at 35 °C.

Stoichiometric Reaction or *n*-Bu_3SnH and Cyclopropylcarbonyl Chloride. The samples were prepared as described for the hexenoyl chloride reaction from 80.5 μL (0.3 mM) of *n*-Bu_3SnH, 27.2 μL (0.3 mM) of c-C_3H_5COCl, 387.3 μL of C_6D_6, and 5 μL of C_6H_6, and the progress of the reaction was monitored by NMR at 35 °C.

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Registry No. *n*-Bu_3SnH, 688-73-3; $C_5H_{11}COCl$, 142-61-0; MeCHO, 75-07-0; EtCHO, 123-38-6; Me_2CHCHO, 78-84-2; Me_3CCHO, 630-19-3; Me_3CCOCl, 3282-30-2; C_5H_9COCl, 36394-07-7; $Me_2CHCOCl$, 79-30-1; EtCOCl, 79-03-8; MeCOCl, 75-36-5; c-C_3H_5COCl, 4023-34-1.