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STUDIES IN GROUP IV ORGANOMETALLIC CHEMISTRY XXIII*. MECHANISM OF THE HYDROSTANNOLYSIS OF TIN–ELEMENT BONDS**

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INTRODUCTION

During the past decade the chemistry of the tin–hydrogen bond has received considerable attention (for recent reviews see refs. 2–4). Whereas originally the main emphasis was on preparative investigations, more recently the mechanistic aspects of organotin hydride chemistry have been studied more closely.

Earlier investigations suggested that hydrostannation reactions (addition reactions of organotin hydrides) proceed preferably by a radical mechanism[3]. However, more detailed mechanistic studies have shown that in hydrostannation reactions either an exclusively ionic mechanism (*e.g.* isocyanates[5] or electrophilic acetylenes[6]) or a combination of an ionic and radical mechanism[6,7], or an exclusively radical mechanism (*e.g.* nucleophilic acetylenes[6]) is operative. In the ionic hydrostannations the organotin hydride hydrogen is transferred as a hydride ion.

The hydrostannolysis of metal–element bonds has been found to be uniquely useful for the synthesis of compounds containing tin–metal bonds[1,8]. We have preliminary reported that the hydrostannolysis of tin–nitrogen[9] and of tin–oxygen[10] bonds proceeds exclusively by an ionic mechanism. In contrast, the hydrostannolysis of carbon–halogen bonds in alkyl halides[11] and acyl halides[12] follows a radical course.

In the present paper the mechanism of reactions of organotin hydrides with tin–element bonds (1) is discussed in greater detail.

$$R_3SnX + R'_3SnH \rightarrow R_3SnSnR'_3 + HX \quad (X = NR_2, PR_2, AsR_2, OR, SR) \quad (1)$$

TIN-NITROGEN HYDROSTANNOLYSIS OF BONDS

Hydrostannolysis reactions of organotin nitrogen derivatives may be conveniently followed by measuring the extinction of the Sn–H stretching frequency in the IR spectrum. We have studied the influence of varying the substituents both at tin and nitrogen, of the polarity of the solvent, and of the presence of radical inhibitors and generators on the reaction rate.

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[*] Part XXII; see ref. 1.

[**] The fission of carbon–element bonds by hydrogen is called "hydrogenolysis". We propose the name "hydrostannolysis" for fission reactions brought about by organotin hydrides.

Representative graphs of our data have been presented in ref. 9. These data clearly demonstrate the negligible effect of added radical scavengers such as phenoxyl* and of free radical generators such as 2,2'-azobisisobutyronitrile (AIBN) on the reaction rate. The results of experiments on substitution and solvent effects are summarized in Table 1. Both effects appear to be pronounced. Replacement of cyclohexane ($\varepsilon = 2.0$) by the more polar butyronitrile ($\varepsilon = 20.3$) in some cases causes the rate to increase by a factor > 100. Electron-withdrawing substituents at nitrogen have a retarding, electron-donating substituents a strongly accelerating effect. Electron-withdrawing groups on the tin atom of the organotin nitrogen compound

TABLE 1

RELATIVE RATES OF THE REACTION $(C_2H_5)_3SnX + R_3SnH \rightarrow (C_2H_5)_3SnSnR_3 + HX$

X	*R = C_6H_5*		*R = p-$CH_3OC_6H_4$*		*R = C_2H_5*	
	Cyclohexane	*Butyronitrile*	*Cyclohexane*	*Butyronitrile*	*Cyclohexane*	*Butyronitrile*
1 $-N(C_6H_4NO_2)CHO$		>100				
2 $-N(C_6H_4Cl)CHO$	0.88					
3 $-N(C_6H_5)CHO$	1.00	>100	0.33			
4 $-N(C_6H_5)NH(C_6H_5)$	1.4					
5 $-N(C_6H_{13})CHO$	10		1.5		<0.08	0.10
6 $-N(n\text{-}C_4H_9)CHO$	12	>100				
7 $-N(tert\text{-}C_4H_9)CHO$	16					
8 $-N(C_2H_5)_2$	>85				0.3	6
9 $-N(C_6H_5)_2$	0.27	>100				
10 $-P(C_6H_5)_2$	0.11[a]	2.9				
11 $-As(C_6H_5)_2$	[b]	0.4				

[a] Hydrostannolysis is accompanied by exchange. [b] Only exchange has been observed.

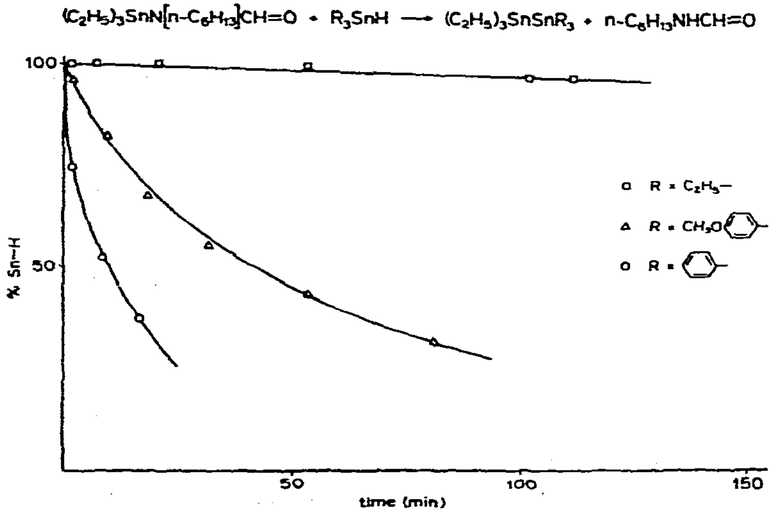

Fig. 1. Reaction of triethyltin(N-hexylformamide) (0.1 *M*) with different hydrides (0.1 *M*) in cyclohexane at 40°.

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* Phenoxyl is a very efficient radical scavenger[26].

also retard the reaction. Replacement of the ethyl groups in triethyl(N-phenylformamido)tin by phenyl groups in the reaction with triphenyltin hydride in butyronitrile reduces the relative rate from > 100 to 1.5. As appears from Fig. 1, substitution at the tin atom of the organotin hydride has the opposite effect, the reaction being slower if the substituents become more electron-donating.

The lack of influence of phenoxyl or AIBN rules out a radical mechanism. Our data are, however, in agreement with an ionic mechanism, the substituent effects pointing to electrophilic attack of the organotin hydride hydrogen on nitrogen.

In order to get a more detailed picture attempts were made to determine the kinetic order of this type of reaction. In each case the reaction rate was found to be a function of the concentration of each of the reactants. Whereas an exact value could not be obtained, our IR results indicate that these reactions are first order in each of the reactants.

Fig. 2 illustrates the dependence of the reaction rate on the concentration of the reactants for the hydrostannolysis of triethyltin diethylamide by triethyltin hydride. The value of the bimolecular rate constant calculated from these data is $\sim 4.10^{-2}$ l·min^{-1}·mol^{-1}.

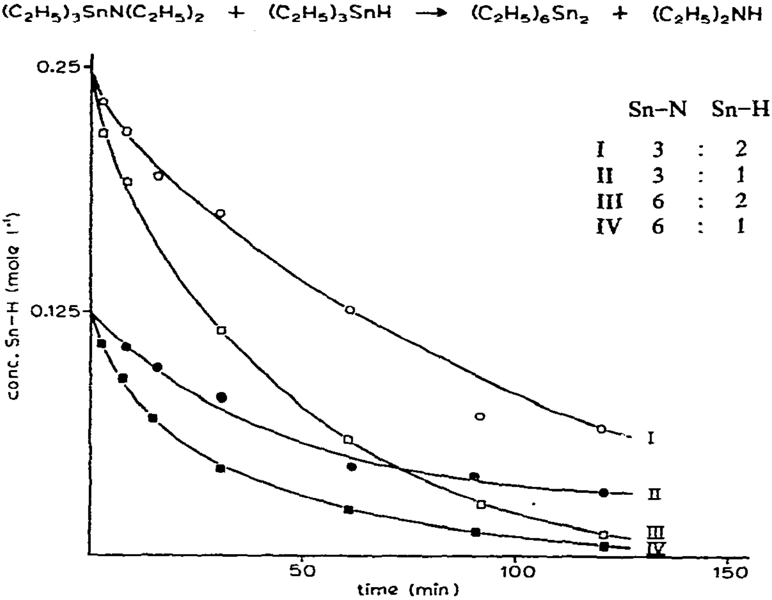

$(C_2H_5)_3SnN(C_2H_5)_2 + (C_2H_5)_3SnH \longrightarrow (C_2H_5)_6Sn_2 + (C_2H_5)_2NH$

Fig. 2. Hydrostannolysis of triethyltin diethylamide with triethyltin hydride in PrCN/C_6H_{12} (1 : 12) at 20°. I, $Et_3SnNEt_2/Et_3SnH = 3:2$; II, 3 : 1; III, 6 : 2; IV, 6 : 1.

The observed first-order kinetics for both reactants rule out a mechanism involving fast or slow dissociation of the organotin hydride as a discrete step (*cf.* ref. 5b). Two possibilities are considered for the bimolecular mechanism:

$$A:\ R_3SnH + R'_3SnNEt_2 \overset{\text{fast}}{\rightleftharpoons} R_3Sn^- + R'_3Sn\overset{+}{\underset{H}{N}}Et_2 \xrightarrow{\text{slow}} R_3SnSnR'_3 + HNEt_2$$

$$B:\ R_3SnH + R'_3SnNEt_2 \xrightarrow{\text{slow}} R_3Sn^- + R'_3Sn\overset{+}{\underset{H}{N}}Et_2 \xrightarrow{\text{fast}} R_3SnSnR'_3 + HNEt_2$$

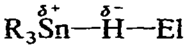
A study of the influence of isotopic substitution in the hydride on the reaction rate has proved to be valuable in elucidating the mechanism of organotin hydride reactions[5,6]. A study of the hydrogen isotope effect allows a choice to be made between A and B.

In mechanism A the hydride hydrogen is attached to nitrogen before the rate-determining step. In that case the ratio k_H/k_D should be smaller than unity (theoretical value ~0.37) as a result of the large difference between the zero-point energies of the Sn–H and the N–H bond.

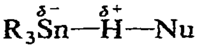
In mechanism B the ratio k_H/k_D may have all values between 3.7 and 0.37, depending on the degree of transfer of the hydrogen from tin to nitrogen in the transition state. The isotope effect k_H/k_D for the reaction of triethyltin diethylamide with triethyltin hydride in cyclohexane/butyronitrile (12:1) at 20° was found to be ~1.2. It follows that mechanism (A) cannot apply and that electrophilic attack of the hydride hydrogen on nitrogen is the first and rate-determining step (mechanism B).

For the reaction of triethyl(N-phenylformamido)tin with triphenyltin hydride second order kinetics (first order in each of the reactants) could be established. Here the ratio k_H/k_D in cyclohexane at 20° was found to be ~2.1.

The following generalizations for ionic organotin hydride reactions appear to be justified. The polarisability of the Sn–H bond plays an important part in this picture. In ionic reactions a transition state is formed in which under the influence of a strong electrophile El the Sn–H bond will become polarized according to (I),


$\mathrm{R_3}\overset{\delta+}{\mathrm{Sn}}—\overset{\delta-}{\mathrm{H}}—\mathrm{El}$

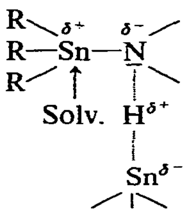
(I)


$\mathrm{R_3}\overset{\delta-}{\mathrm{Sn}}—\overset{\delta+}{\mathrm{H}}—\mathrm{Nu}$

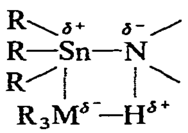
(II)

and under the influence of a strong nucleophile Nu according to (II). Phenyl and other electron-attracting groups on tin allow delocalization of partial negative charge on tin and thus favor electrophilic attack by the hydride according to (II). Electron-donating alkyl groups increase the electron density on tin and thus promote the nucleophilic attack by the hydride according to (I). This explains why in every respect reversed reactivity sequences have been observed for the *nucleophilic* hydrostannation of isocyanates and isothiocyanates[5] and for the *electrophilic* hydrostannolysis of organotin nitrogen compounds discussed in this paper.

Similarly, proton transfer from germanium to nitrogen has been proposed as the rate-determining step in the corresponding organogermane reactions[1]. Triethyltin diethylamide reacts approximately one thousand times slower with triphenylgermane than with triphenyltin hydride. The activation energy connected with the proton transfer will be considerably greater for the germane than for the tin hydride. Whereas the rate of hydrostannolysis reactions may be increased by a factor of ~100 by changing the solvent (Table 1), triphenylgermane reacts with triethyltin diethylamide in butyronitrile only ~6 times faster than in cyclohexane. Apparently stabilization of ionic intermediates by the solvent is of greater importance for the tin hydride than for the germanium hydride reactions. However, the stabilization of anionic triphenyltin or triphenylgermyl species by an electron-donating solvent does not seem to be a likely process. The cationic species which may be expected to be stabilized by butyronitrile are identical for both reactions.



S_E2; in polar solvents



S_F2; in non-polar solvents and the reaction with triphenylgermane

Therefore, we prefer to accept a four-centre type reaction (S_F2 mechanism) for the triphenylgermane reaction. Such a mechanism may also be operative in hydrostannolysis reactions in non-polar solvents. Our results in polar solvents are best explained in terms of an S_E2 mechanism involving nucleophilic assistance of the solvent. Similar mechanisms have been proposed for the reactions of tin tetraalkyls with halogens[13] and for the cleavage by iodine of the tin–tin bond in hexaalkylditin compounds[14].

The reactivity of the tin–phosphorus and tin–arsenic bond in the hydrostannolysis reaction has been investigated for comparative purposes. Triethyltin diphenylphosphide and diphenylarside were found to be appreciably less reactive towards triphenyltin hydride than triethyltin diphenylamide (see Table 1). This is best explained in terms of decreased nucleophilic character of the phosphide and arside substituents as compared with the diphenylamino group. The occurrence of d_π–p_π bonding would result in reduced availability of the non-bonding electron pair and hence in reduced reactivity. Such π-bonding might be expected to be of greater importance for the phosphide and arside than for the amide because of the more favorable size relationship of the orbitals involved (dipole moment studies of these compounds are consistent with this tendency[15]).

The occurrence of a competitive exchange reaction with the phosphino- and arsinotin compound will be discussed in a separate section of this paper.

HYDROSTANNOLYSIS OF THE TIN–OXYGEN BOND

The influence of substitution, of the polarity of the solvent and of radical generators and scavengers on the rate of hydrostannolysis of organotin–oxygen derivatives has been investigated (IR spectroscopic method).

Representative graphs of our rate data have been presented in ref. 10. These results have been summarized in Table 2 (k-values relative to reaction 3, Table 1).

Electron-donating substituents at oxygen have an accelerating effect as appears from a comparison of the rates for organotin alkoxides and phenoxides. This is further illustrated by the rates observed for a number of *para*-substituted phenoxides where a good correlation with the Hammett σ-constants of the substituents is observed (Fig. 3).

The influence of substitution at the tin atom of the hydride appears to be opposite, electron-donating substituents having a retarding effect. The rate of reaction with triethyltin phenoxide increases in the sequence $Et_3SnH < (p\text{-}MeOC_6H_4)_3SnH < Ph_3SnH$ (*cf.* ref. 10).

TABLE 2

RELATIVE RATES OF THE REACTION: $(C_2H_5)_3SnOR + (C_6H_5)_3SnH \rightarrow (C_2H_5)_3SnSn(C_6H_5)_3 + ROH$

	OR	*Cyclohexane*	*Cyclohexane/ butyronitrile* 9 : 1	*Butyronitrile*
1	$-O-C_6H_4-NO_2$-*p*	<0.1		0.35
2	$-O-C_6H_4-Cl$-*p*	0.16		1.1
3	$-OC_6H_5$	0.26		1.4
				0.48[c]
4	$-O-C_5H_4-OCH_3$-*p*			2.8
5	$-O-C(CH_3)_3$	0.52	5.0	>50
6	$-O-CH(CH_3)-CH_2-CH_3$	[a]	3.7	>50
7	$-O-CH_2-CH_3$	[b]	[a]	>50
8	$-O-CH_3$	[b]		
9	$-O-CH_2-C_6H_5$	[a]	3.7	20
10	$-S-C_4H_9$	[b]		<0.1

[a] Hydrostannolysis and exchange occur simultaneously. [b] Only exchange has been observed. [c] Reaction with tris(*p*-methoxyphenyl)tin hydride.

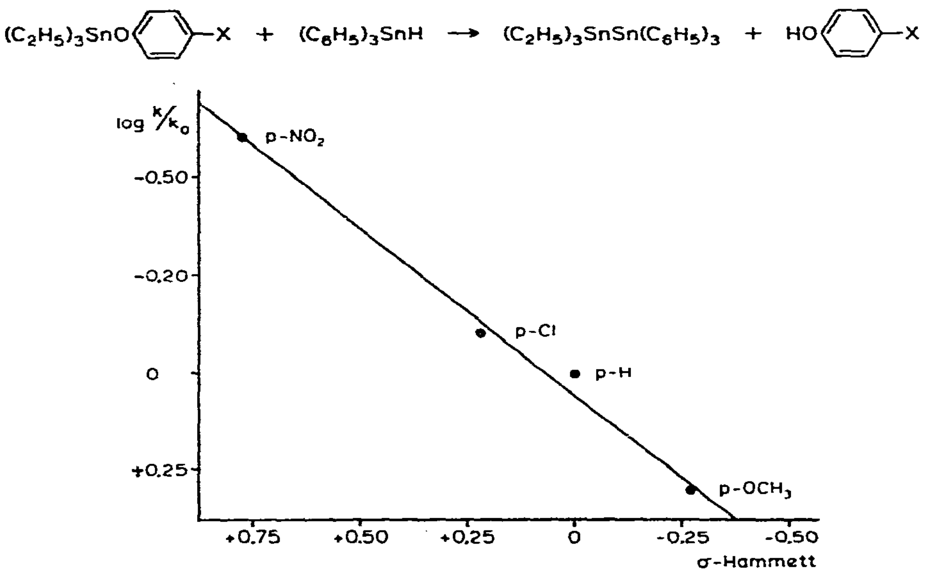
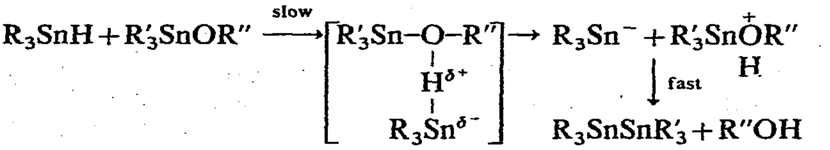


Fig. 3. Correlation of reaction rate and Hammett σ-constants for the reaction of *p*-substituted organotin phenoxides and triphenyltin hydride.

The observed lack of influence of phenoxyl and of AIBN (ref. 10) and the considerable solvent effect point to an ionic mechanism. The influence of substitution on the rate is in agreement with electrophilic attack of the organotin hydride hydrogen on oxygen. The following S_E2 mechanism is proposed:



$$R_3SnH + R'_3SnOR'' \xrightarrow{\text{slow}} \left[\begin{array}{c} R'_3Sn{-}O{-}R'' \\ | \\ H^{\delta+} \\ | \\ R_3Sn^{\delta-} \end{array}\right] \rightarrow R_3Sn^- + R'_3Sn\overset{+}{O}R'' \atop \overset{}{\downarrow}{\scriptstyle\text{fast}}\quad H$$

$$R_3SnSnR'_3 + R''OH$$

If hydrostannolysis is slow as *e.g.* with triethyltin methoxide in a non-polar solvent a competitive exchange reaction takes place (see below).

EXCHANGE REACTIONS INVOLVING ORGANOTIN HYDRIDES

In addition to the hydrostannolysis reaction (1) an exchange reaction of type (2) may occur between triorganotin hydrides and organotin compounds containing a tin–element bond.

$$R_3SnX + R'_3SnH \rightleftarrows R_3SnH + R'_3SnX \qquad (2)$$

Many examples of this reaction have been mentioned in the literature, *e.g.* X = halogen[16,17]; RCOO[18], D[19], OR[10], SR[10], and notably in a very recent publication[20] (X = $OSnR_3$, $SSnR_3$, CN and PR_2).

In most of the reactions involving organotin–nitrogen compounds discussed in the present paper hydrostannolysis (1) is so much faster than exchange (2) that reaction (2) is not observed. For organotin thioalkoxides (X = SR)[10] and for a number of organolead–oxygen and –nitrogen derivatives[21] (2) is fast with respect to (1) and exchange is the only reaction. However, for the reaction of Et_3SnPPh_2 and $Et_3SnAsPh_2$ and a number of triorganotin alkoxides with Ph_3SnH the rates of (1) and (2) are of the same order and a mixture of products is formed.

The nature of the exchange reaction was investigated more closely (X = NRR′, OR and PR_2) using NMR spectroscopy. A mixture containing different organotin hydrides may be readily analyzed because the chemical shift of protons directly bound to tin varies with substitution at tin[22,23]. Some of our results are summarized in Table 3.

TABLE 3

EXCHANGE REACTIONS BETWEEN ORGANOTIN HYDRIDES AND ORGANOTIN ELEMENT COMPOUNDS AT 40°

	Et_3SnX	*R_3SnH*	*In cyclohexane*		*In butyronitrile*	
			Et_3SnH	*R_3SnH*	*Et_3SnH*	*R_3SnH*
1	$Et_3SnN(Ph)C(O)H$	Me_3SnH	50%	50%	53%	47%
2	$Et_3SnN(Ph)C(O)H$	Ph_3SnH	0	^{a}		
3	Et_3SnNEt_2	Me_3SnH	0	^{a}	23	77
4	Et_3SnNPh_2	Me_3SnH	0	100	10	90
5	Et_3SnPPh_2	Me_3SnH	60	40	47	53
6	Et_3SnPPh_2	Ph_3SnH	40^b	^{a}	34^b	^{a}
7	Et_3SnOMe	Me_3SnH	60	40	67	33
8	Et_3SnOPh	Me_3SnH	50	50		
9	Et_3SnOPh	Ph_3SnH	<20%	^{a}	<20%	^{a}

[a] Amount of hydride not determined. [b] Determined by means of an internal standard (hexamethylditin).

As might be expected substitution at tin and at the hetero atom largely influences the extent of exchange. In reactions which have preferably been applied to the synthesis of tin–tin bonds (reaction 2[8a], 3[8c] and 4 of Table 3) the occurrence of exchange could not be detected by NMR. This observation, which is corroborated by the results of unpublished experiments, does not agree with the mechanism proposed by Neumann *et al.*[20,24] for the formation of polystannanes from organotin hydrides and diethylaminotin compounds, in which exchange plays an important part. Exchange predominates if the hetero atom is a second or third row element (S, P, As).

It appears that reactions of type (2) are equilibrium reactions. The position of the equilibrium does not vary very much with the polarity of the solvent. A four-center type mechanism seems indicated (*cf.* ref. 10 and 20) in which the organotin hydride now acts as a nucleophile.

EXPERIMENTAL PART

Since the organometallic compounds used in this study are air-sensitive, all manipulations were carried out in an atmosphere of dry nitrogen. Cyclohexane was distilled before use from $LiAlH_4$ in an inert atmosphere. Butyronitrile was distilled three times from P_2O_5 and once under nitrogen from K_2CO_3. The organotin compounds used in this study were prepared according to published procedures.

Triethyl(N-butylformamido)tins (n- and tert-butyl) were prepared by a transamination reaction of triethyltin diethylamide with the appropriate formamido compound[25].

Triethyl- and triphenyltin deuteride were prepared from diethylaluminium deuteride and the appropriate organotin chloride following partly the method described by Leusink *et al.*[5b].

Hydrostannolysis reactions

The experiments were carried out in a small reaction flask containing 1 mmol of the organotin hydride and 1 mmol of the organotin hetero compound in 5 or 10 ml of the solvent. The rate of reaction was determined by measuring the intensity of the Sn–H stretching frequency at about 1800 cm^{-1} (Sn–D at about 1300 cm^{-1}) in the IR spectrum, using a Perkin–Elmer Infracord 137 spectrophotometer or a Grubb Parson Spectromaster.

At appropriate time intervals samples were taken from the solution, which was kept in a constant temperature bath ($\pm 0.2°$).

Exchange reactions

Solutions of 0.4 mmol of an organotin hydride and 0.4 mmol of an organotin hetero compound in 400 μl of a solvent were mixed in an NMR tube, and the NMR spectrum was recorded at 40° using a Varian Associates HR 100 NMR spectrometer.

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SUMMARY

The mechanism of the reaction of organotin hydrides with compounds

containing a tin–element bond (Sn–N, Sn–P, Sn–As, Sn–O, Sn–S) has been investigated using IR spectroscopic techniques. In reactions involving formation of a tin–tin bond (hydrostannolysis reactions) a polar mechanism is operative as appears from the lack of activity of free radical generators or scavengers and from the influence of the polarity of the solvent on the rate of reaction. Kinetics, isotope effect and the influence of substituents attached to tin and nitrogen on the rate of hydrostannolysis of organotin–nitrogen derivatives indicate electrophilic attack of the organotin hydride hydrogen on nitrogen as the first and rate-determining step. Substituent effects strongly favor an identical mechanism for the hydrostannolysis of organotin–oxygen derivatives.

Exchange reactions predominate hydrostannolysis, if the hetero atom is a second or third row element (S, P, As). The nature of this reaction, which has been studied more closely for organotin–nitrogen derivatives using NMR spectroscopy, is discussed.

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