Journal of Organometallic Chemistry, 85 (1975) 335—346

REACTIONS OF HEXAMETHYLDITIN WITH ALKYLMERCURY SALTS

I. STOICHIOMETRY AND RATE STEP

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(Received September 3rd, 1974)

Summary

Hexamethylditin in methanol solution reacts rapidly with mercuric chloride to yield mercury and trimethyltin chloride. With alkylmercuric salts the reaction is complex, yielding tetraalkyltin and/or dialkylmercury, depending upon the reactivity of the alkylmercuric salt. An electrophilic substitution mechanism involving trimethylstannyl mercurials as transient intermediates is suggested. The reaction of hexaalkylditin with diarylmercury is suggested to follow a homolytic pathway.

Introduction

In order to investigate the effect of substituents on the tin chemical shifts of trimethylaryltins [1] we wished to prepare the *m*- and *p*-nitrophenyl derivatives. However, the conventional Grignard route to these compounds is inapplicable, as indeed is the case for all the powerfull electron-withdrawing groups with the exception of trifluoromethyl. An attractive route is suggested by reactions 2 and 3 of the following scheme reported by Kocheshkov, Nesmeyanov and Pusyreva [2] since the nitrophenylmercurials are obtainable through the aryldiazonium salt decomposition route [3].

$$R_6Sn_2 + HgCl_2 \xrightarrow[0.5\ h]{150^\circ} Hg + 2R_3SnCl \qquad (1)$$

$$R_6Sn_2 + R'HgCl \xrightarrow[3\ h]{150^\circ} Hg + R_3SnCl + R_3SnR' \qquad (2)$$

$$R_6Sn_2 + R'_2Hg \xrightarrow[7\ h]{170^\circ} Hg + 2R_3SnR' \qquad (3)$$

The reactions reported were conducted in the absence of solvent and had $R = C_2H_5$ and R' = various aryl groups. The yields of mercury produced were of the order of 90%, while the yields of R_3SnR' products varied apparently according to the difficulty of their isolation, suggesting that the reactions themselves might be close to quantitative. On the other hand our experience suggests that the conditions employed for reactions 1 and 2 were excessively strenuous.

Since the reactions are also of interest as possible examples of electrophilic tin—tin bond cleavage, although this appears unlikely in the case of reaction 3, we have examined reaction 1 and particulalrly reaction 2 in order to establish their mechanism and scope. In this paper we report on the stoichiometry and kinetics of a number of reactions and we suggest a possible mechanism. In the following paper we examine decomposition routes of the postulated intermediates [23].

Experimental

Materials

Hexamethylditin (Alfa Inorganics) was purified by distillation under reduced pressure with a nitrogen bleed. Small samples (ca. 0.25 g) were sealed under vacuum in ampoules flushed with dry nitrogen and the ampoules stored in a refrigerator. Tetramethyltin (Alfa Inorganics) was distilled at atmospheric pressure immediately before use. Trimethyl-t-butyltin was prepared by reaction of trimethyltin chloride with t-butyllithium in pentane (cf. ref. 4). Purification by distillation under reduced pressure yielded a low melting solid, m.p. 30° (Lit. [4] 31.5°). Trimethylvinyltin was prepared according to ref. 4. Trimethyltin chioride (Alfa Inorganics) was purified by distillation at atmospheric pressure. Mercuric chloride (analytical reagent grade UNIVAR), mercuric bromide (Hopkins and Williams Fine Chemicals), mercuric iodide, cyanide and acetate (reagent grade BDH) were used without further purification.

Methylmercuric iodide was synthesized by the Grignard procedure [6] and purified by sublimation. Other methylmercuric salts were obtained from the iodide by metathetical reactions and purified either by crystallisation or by sublimation. Methylmercuric cyanide was kindly donated by Dr. J.R. Hall. Trideuteromethylmercuric chloride was prepared from trideuteromethyl iodide by the Grignard procedure yielding the iodide followed by metathesis as above.

trans-Chlorovinylmercuric chloride was prepared from acetylene by the method of Nesmeyanov and Freidlina [7] and converted to bis(*trans*-2-chlorovinyl)mercury by reaction in benzene solution with ammonia [7]. Both were purified by crystallisation. Vinylmercuric chloride was prepared from tetravinyltin (M & T Chemicals) as described by Seyferth [8] and purified by crystallisation. t-Butylmercuric chloride was prepared from t-butylmagnesium chloride (Alfa Inorganics) in anhydrous ether [9] and purified by sublimation.

Methanol (analytical reagent grade UNIVAR) was further purified by distillation from magnesium methoxide and stored over Type 3A molecular sieves. The solvent was degassed on a vacuum line by the "freeze-thaw" technique immediately before use.

The purity of all the organometallic compounds was carefully checked by examination of their PMR spectra at high gain.

TABLE 1

METHYL GROUP RESONANCES[a]

	$\delta(CH_3)$[b] (ppm)	J[c] (Hz)
$(CH_3)_6Sn_2$	0.20	50; 48 (Sn—C—H) 16; 15.5 (Sn—Sn—C—H)
$(CH_3)_4Sn$	0.06	54; 51.5
$(CH_3)_3SnCl$	0.60	67.5; 64.5
$(CH_3)_3SnC(CH_3)_3$	0.00	57; 54.5 (Sn—C—H)
$(CH_3)_3SnC(CH_3)_3$	1.07	66; 63 (Sn—C—C—H)
$(CH_3)_2SnC(CH_3)_3Cl$	0.52_5	57; 54.5 (Sn—C—H)
$(CH_3)_2SnC(CH_3)_3Cl$	1.24_5	90; 86 (Sn—C—C—H)
$(CH_3)_2Hg$	0.22	104
CH_3HgCl	0.95	210

[a] In methanol. [b] Chemical shifts positive to low field of TMS. [c] Scalar coupling between protons and ^{119}Sn, ^{117}Sn or ^{199}Hg.

Product examination

With the exception of metallic mercury, all products were identified by their PMR spectra in some cases measured at both 60 MHz (Varian A-60) and 100 MHz (JEOL PS-100 or MH-100) with the addition of authentic samples for confirmation. Table 1 summarises the methyl group resonances observed in these studies. Spectra were examined at high gain for minor products.

Kinetic measurements

The following general procedure was employed.

Standard solutions typically ca. 0.2 *M* of hexamethylditin and the reagent in methanol were prepared in 5 ml standard flasks. By means of a syringe 0.3 ml of the reagent was added to a previously weighted NMR tube fitted with a pressure cap, and the tube reweighed. After equilibration to the probe temperature 0.3 ml of the hexamethylditin solution was added to the tube, which was tightly restoppered and vigorously shaken for about thirty seconds before being replaced in the probe. The amount of hexamethylditin added was determined by weighing the tube at the completion of the experiment. Following the examination of trial mixtures, it was found that concentrations could be related to peak heights with appropriate corrections for isotopic composition. The procedure was also checked for the individual reactants employing either cyclohexane or the high field ^{13}C satellite of methanol as references and found to be satisfactory.

Figure 1 illustrates one of the more complex spectra employed, arising from a reaction of approximately equal initial concentrations of methylmercuric chloride and hexamethylditin. Five species are clearly observable at this stage, although at earlier reaction times the low concentration of dimethylmercury must be estimated indirectly by:

$$[(CH_3)_2Hg]_t = \tfrac{1}{2}\,\{[(CH_3)_3SnCl]_t - [(CH_3)_4Sn]_t\}$$

No discontinuity was observed where the change-over from indirect to direct estimation took place.

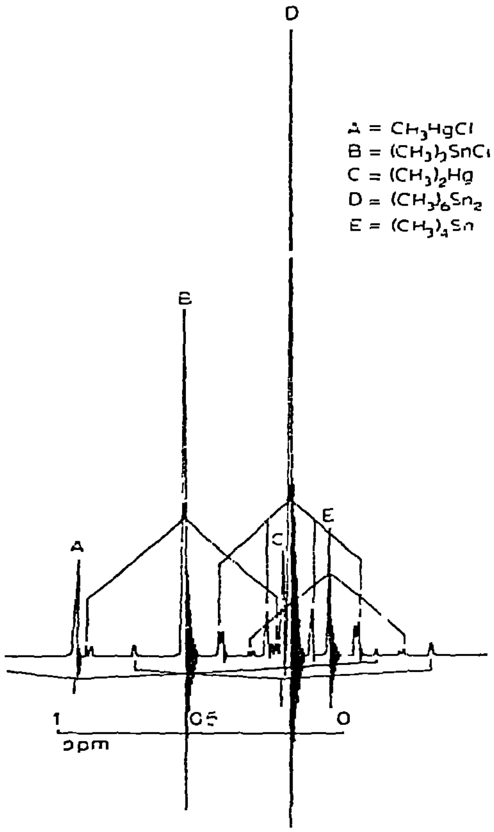

Fig. 1. 100 MHz NMR spectrum of reaction mixture (C1).

After commencement of the reaction, portions of the spectral region shown in Fig. 1 were scanned (1 Hz s^{-1}) at one minute intervals. In most cases peak B and then peaks C, D and E together were recorded. Peak A arising from methylmercuric chloride is always small and the concentration of this species is best obtained from:

$$[CH_3HgCl]_0 - [CH_3HgCl]_t = [(CH_3)_3SnCl]_t$$

The data thus obtained were subjected to a 'smoothing' treatment by the method of moving averages to eliminate some of the random scatter arising from the method of analysis*. In this treatment each piece of data during a sequence of equal time intervals was modified to the mean of itself and the data immediately preceding and following it. Thus were obtained concentration vs. time curves as illustrated in Fig. 2.

Typically reactions were followed to ca. 75% completion occupying some sixty minutes.

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* The measurement of peak heights in PMR spectra provides a rather moderate method of analysis, but we were able to obtain a large number of data points for several species in a relatively short time and specify the kinetic curves quite satisfactorily.

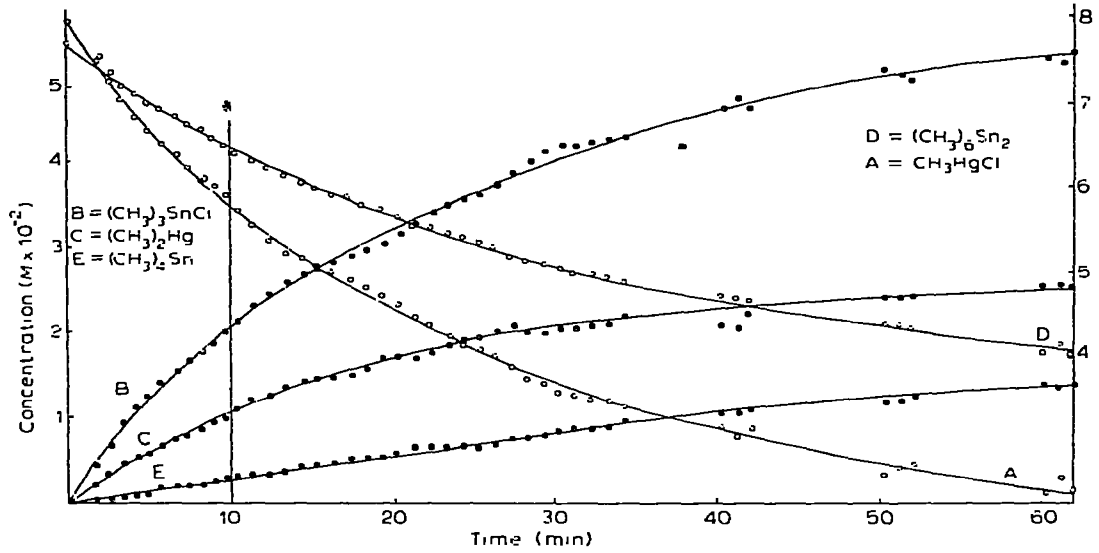

Fig. 2. Concentration—time curves for the reaction (C1). (*Change over point for $(CH_3)_2Hg$ analysis.)

The majority of kinetic experiments were carried out using the JEOL PS-100 spectrometer in the internal lock mode using the hydroxyl signal of methanol for the lock. The temperature of the probe was either 30 ± 1°, as measured by a calibrated thermocouple, or, for the kinetic experiments at 60 MHz, the probe temperature was 35 ± 1°.

Results

Hexamethylditin with mercuric chloride

Hexamethylditin (ca. 0.1 *M*) reacted quantitatively with mercuric chloride (ca. 0.1 *M*) in methanol solution at room temperature in less than one minute according to eqn. 4. The mercury formed very cleanly, and rapidly collected

$$(CH_3)_6Sn_2 + HgCl_2 \rightarrow 2\ (CH_3)_3SnCl + Hg \qquad (4)$$

into a drop at the bottom of the tube without interfering with the observation of the spectrum. Only trimethyltin chloride was observed as a product accompanying hexamethylditin when the latter was in excess. (There is a subsequent very slow decomposition of hexamethylditin catalysed by trimethyltin chloride [10].) When mercuric chloride is in slight excess the residue becomes converted to mercurous chloride. The reaction of trimethyltin chloride with mercuric chloride occurs quite slowly, $1.3 \times 10^{-3}\ M^{-1}\ s^{-1}$ (30°), yielding dimethyltin dichloride and methylmercuric chloride.

Hexamethylditin (0.170 *M*) and tetramethyltin (0.227 *M*) in methanol containing cyclohexane (0.241 *M*) as internal reference were reacted with mercuric chloride (0.104 *M*) at 30°. The unreacted hexamethylditin was 0.078 *M* whereas 0.066 *M* would have been expected for complete reaction. The difference corresponds to ca. 4% of the tetramethyltin undergoing reaction. The concentrations of tetramethyltin and trimethyltin chloride were within 5% of expectation but are rather insensitive probes of the system. Methylmercuric chloride (0.012 M expected) was in insufficient concentration to be detected with certainty. This result corresponds to a rate of reaction 4 relative to tetramethyltin (TMT) of $k_4/k_{\mathrm{TMT}} \approx 15$. A second experiment with initial concentrations $[(CH_3)_6Sn_2]_0$ 0.161 M, $[(CH_3)_4Sn]_0$ 0.206 M and $[HgCl_2]_0$ 0.095 M gave $k_4/k_{\mathrm{TMT}} \approx 20$.

Trimethyl-t-butyltin with mercuric chloride

For concentrations of both reactants of ca. 0.1 M in methanol reaction is complete in less than one minute at ca. 30° yielding only methylmercuric chloride and dimethyl-t-butyltin chloride. Trimethyltin chloride and t-butylmercuric chloride could not be detected in the product.

Hexamethylditin with methylmercuric chloride

The reaction of hexamethylditin with methylmercuric chloride yields the products expected for reaction 2 but not in the anticipated proportions, and in addition dimethylmercury is obtained according to the stoichiometry of eqn. 5, in which the quantity x varies during the course of any reaction and depends upon the relative concentrations of the reactants.

$$(CH_3)_6Sn_2 + (1+x)\,CH_3HgCl \rightarrow (1+x)\,(CH_3)_3SnCl + (1-x)\,(CH_3)_4Sn + x(CH_3)_2Hg + Hg \quad (5)$$

As illustrated in Fig. 2, initially the rate of production of dimethylmercury is greater than that of tetramethyltin, but as the reaction proceeds these rates become comparable with tetramethyltin production almost linear with time.

When methylmercuric chloride (0.076 M) is initially present in large excess over hexamethylditin (0.019 M), tetramethyltin becomes a relatively insignificant product, ca. 5% of $[(CH_3)_2Hg]$, and the reaction essentially follows eqn. 6.

$$(CH_3)_6Sn_2 + 2\,CH_3HgCl \rightarrow 2(CH_3)_3SnCl + (CH_3)_2Hg + Hg \quad (6)$$

Under these conditions eqn. 7 is a good approximation for the integrated form of the kinetic expression,

$$\ln\left\{\frac{[(CH_3)_6Sn_2]_t}{[CH_3HgCl]_0 - [(CH_3)_3SnCl]_t}\right\} = \ln\left\{\frac{[(CH_3)_6Sn_2]_t}{[CH_3HgCl]_t}\right\} = tk_{\mathrm{obs}}\{2[(CH_3)_6Sn_2]_0 - [CH_3HgCl]_0\} + \ln\left\{\frac{[(CH_3)_6Sn_2]_0}{[CH_3HgCl]_0}\right\} \quad (7)$$

yielding $k_{\mathrm{obs}} = 5.2 \times 10^{-3}\ M^{-1}\ s^{-1}$ (30°). This is illustrated in Fig. 3.

The rate data were also examined in terms of the kinetic expression 8, but

$$-d[(CH_3)_6Sn_2]/dt \propto [CH_3HgCl]^2 \quad (8)$$

this was found to be quite unsatisfactory.

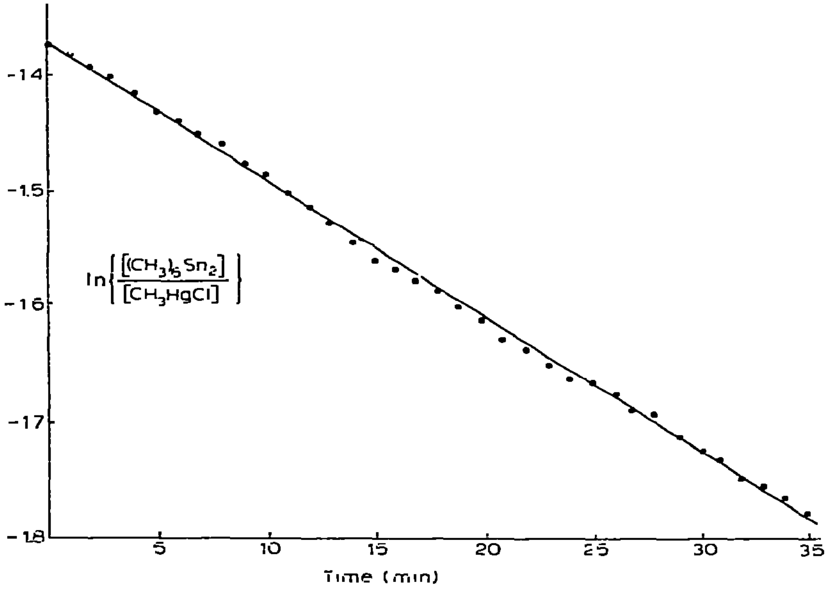

Fig. 3. Second order plot for reaction system C4.

Hexamethylditin with trideuteromethylmercuric chloride

Under reaction conditions where dimethylmercury is the predominant product and tetramethyltin production is very small, the methyl groups initially present in hexamethylditin are all found in trimethyltin chloride, and the CD_3-group remains bonded to mercury as expressed in eqn. 9.

$$(CH_3)_6Sn_2 + 2\ CD_3HgCl \rightarrow 2(CH_3)_3SnCl + (CD_3)_2Hg + Hg \qquad (9)$$

No resonances arising from $(CH_3)_2Hg$, CH_3HgCD_3 nor CH_3HgCl could be detected.

Hexamethylditin with other methylmercuric salts

Methylmercuric acetate is considerably more reactive than methylmercuric chloride and the product composition is essentially that expected from eqn. 6, i.e. with no detectable tetramethyltin formation. The reaction is essentially complete in less than 2 min for 0.01 *M* reagents.

Methylmercuric iodide reacts more slowly and yields predominantly tetramethyltin. For a large part of the kinetic run, particularly with hexamethylditin in excess, the rate data corresponds closely to a second order process (eqn. 10).

$$(CH_3)_6Sn_2 + CH_3HgI \rightarrow (CH_3)_3SnI + (CH_3)_4Sn + Hg \qquad (10)$$

Methylmercuric bromide resembles methylmercuric chloride both in rate and product composition although tetramethyltin formation is more important. Dimethylmercury production quickly levels off and the rate data for the later period of the reaction could be processed as described for the methylmercuric iodide reaction.

TABLE 2

REACTIONS OF HEXAMETHYLDITIN WITH METHYLMERCURIC SALTS[a]

Salt	k_{obs} (M^{-1} s^{-1})	Products
Acetate (30°)	>7.5[b]	$(CH_3)_2Hg$
Chloride (30°)	5.2×10^{-3}	$(CH_3)_2Hg + (CH_3)_4Sn$
Bromide (33°)	3.8×10^{-3}	$(CH_3)_4Sn + (CH_3)_2Hg$
Iodide (33°)	2.5×10^{-3}	$(CH_3)_4Sn$
Cyanide (50°)	5×10^{-6}	$(CH_3)_2Hg$

[a] In methanol. [b] Reaction > 90% complete in two minutes.

Methylmercuric cyanide reacts extremely slowly yielding only dimethylmercury and trimethyltin cyanide. Rate measurements were carried out at 50°.

Table 2 summarises the rate and product composition data of these reactions.

Hexamethylditin with vinylmercuric chloride

Hexamethylditin (0.073 *M*) reacts with vinylmercuric chloride (0.162 *M*) in methanol at 35° according to eqn. 11, with a second order rate constant

$$(CH_3)_6Sn_2 + 2\,CH_2{=}CHHgCl \rightarrow 2(CH_3)_3SnCl + (CH_2{=}CH)_2Hg + Hg \qquad (11)$$

$k_{obs} = 6.3 \times 10^{-3}\ M^{-1}\ s^{-1}$. Trimethylvinyltin, tetramethyltin and methylvinylmercury could not be detected in the product. The data cannot be fitted to expressions corresponding to rate controlling nor equilibrium formation of divinylmercury and mercuric chloride.

Hexamethylditin with trans-2-chlorovinylmercuric chloride

The reaction of hexamethylditin (0.16 to 0.09 *M*) with *trans*-2-chlorovinylmercuric chloride (0.14 to 0.18 *M*) in methanol at 35° conforms to the equivalent of eqn. 11 with $k_{obs} = 1.57\ (\pm\ 0.6) \times 10^{-2}\ M^{-1}\ s^{-1}$ (mean of three runs). No other products could be detected.

The reaction proceeds with the same rate constant, $1.63 \times 10^{-2}\ M^{-1}\ s^{-1}$, for hexamethylditin (0.136 *M*), *trans*-2-chlorovinylmercuric chloride (0.143 *M*) and bis(*trans*-2-chlorovinyl)mercury (0.155 *M*).

Hexamethylditin with phenylmercuric acetate

At 20° phenylmercuric acetate (0.01 *M*) reacts rapidly with hexamethylditin (0.01 *M*) with a second order rate constant of 0.1 $M^{-1}\ s^{-1}$ to yield exclusively diphenylmercury, trimethyltin acetate and unreacted hexamethylditin.

Tetramethyltin with methylmercuric chloride

After 80 min at 30° in methanol with methylmercuric chloride (0.128 *M*) there is a 10% conversion of tetramethyltin (0.279 *M*) to trimethyltin chloride and dimethylmercury. The second order rate constant was found to be $1.8 \times 10^{-4}\ M^{-1}\ s^{-1}$.

Trimethylvinyltin with vinylmercuric chloride

Trimethylvinyltin (0.089 *M*) reacts with vinylmercuric chloride (0.127 *M*) in methanol at 35° to yield trimethyltin chloride and divinylmercury rapidly such that 75% of the trimethylvinyltin is consumed in five minutes. The second order rate constant was found to be 0.1 $M^{-1}\ s^{-1}$.

Trimethyl-t-butyltin with methylmercuric chloride

Reaction proceeds very slowly at 30°, $k_{obs} = 3.5 \times 10^{-5}\ M^{-1}\ s^{-1}$, yielding exclusively dimethylmercury and dimethyl-t-butyltin chloride.

Hexamethylditin with t-butylmercuric chloride

No reaction was detected between hexamethylditin (0.221 M) and t-butylmercuric chloride (0.142 M) in methanol after 50 h at 30°.

Discussion

As suspected, reaction 1 proceeds very rapidly and the conditions previously described are unnecessarily severe.

The simplest mechanism for the reaction of hexamethylditin with mercuric chloride involves electrophilic tin—tin bond cleavage with the formation of an unstable trimethylstannyl mercurial (eqn. 12). The corresponding intermediate is presumably formed from the reactions of bis(trimethylsilyl)mercury [11] and of bis(triethylgermyl)mercury [12] with mercuric salts where the corresponding products are obtained.

$$\begin{array}{l}(CH_3)_6Sn_2 + HgCl_2 \rightarrow (CH_3)_3SnHgCl + (CH_3)_3SnCl \\ \qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad (CH_3)_3SnCl + Hg\end{array} \tag{12}$$

This is contrary to the behaviour of hexaphenyldilead [13] and hexaphenylditin [14] where carbon—metal cleavage is preferred, but parallels the case of hexamethyldilead [15, 16].

The instability of intermediates of this type most reasonably arises from the facile nucleophilic attack of chloride on tin in the ion pair $(CH_3)_3SnHg^+Cl^-$.

Electrophilic tin—carbon cleavage would not yield the observed products but would instead lead to methylmercuric chloride and/or dimethylmercury unless the following set of reactions took place:

$$\begin{array}{l}(CH_3)_6Sn_2 + HgCl_2 \rightarrow (CH_3)_5Sn_2Cl + CH_3HgCl \\ (CH_3)_5Sn_2Cl \rightarrow (CH_3)_3SnCl + [(CH_3)_2Sn] \\ [(CH_3)_2Sn] + CH_3HgCl \rightarrow (CH_3)_3SnCl + Hg\end{array} \tag{13}$$

with these the *only* reactions taking place. It is necessary that the pentamethylditin species does not react further with mercuric chloride and that the dimethyltin intermediate reacts exclusively with methylmercuric chloride.

A further argument against tin—carbon cleavage follows from the slower reactions of tetramethyltin and trimethyl-t-butyltin, whose reactivity would be anticipated to be somewhat faster and somewhat slower, respectively, than that of hexamethylditin. The high reactivity in the present case is clearly associated with the presence of a tin—tin bond. Table 3 indicates that this applies to reaction both with mercuric chloride and with methylmercuric chloride.

TABLE 3

MERCURIC CHLORIDE AND METHYLMERCURIC CHLORIDE REACTIONS[a]

Substrate	$HgCl_2$		CH_3HgCl	
	Rate constant (M^{-1} s^{-1})	Cleavage	Rate constant (M^{-1} s^{-1})	Cleavage
$(CH_3)_6Sn_2$	$2k \approx 30$	Sn—Sn	$2k$ 5.2×10^{-3}	Sn—Sn
$(CH_3)_3SnC(CH_3)_3$		Sn—CH_3[b]	$3k$ 3.5×10^{-5}	Sn—CH_3[b]
$(CH_3)_4Sn$	$4k$ 2.0[c]	Sn—CH_3	$4k$ 1.8×10^{-4}	Sn—CH_3
$(CH_3)_3SnCl$	$3k$ 1.3×10^{-3}	Sn—CH_3	$3k \approx 10^{-7}$	Sn—CH_3

[a] In methanol; 30°. [b] No detectable Sn—$C(CH_3)_3$ cleavage. [c] 1.55 M^{-1} s^{-1} at 25° [17].

A mechanism for the reaction of hexamethylditin with methylmercuric chloride which would have the observed kinetic form, yield the observed produc in a ratio dependent upon the composition of the system in the observed manne and parallel eqn. 12 above, is summarised in eqn. 14 for the general case, in

$$(CH_3)_6Sn_2 + RHgX \xrightarrow{a} (CH_3)_3SnX + (CH_3)_3SnHgR \qquad (14a)$$

$$(CH_3)_3SnHgR \xrightarrow{b} (CH_3)_3SnR + Hg \qquad (14b)$$

$$(CH_3)_3SnHgR + RHgX \xrightarrow{c} (CH_3)_3SnX + R_2Hg + Hg \qquad (14c)$$

which reactions b and c are rapid relative to reaction a [$(CH_3)_3SnHgR$ is not observed in any of the systems studied].

Again the reaction must proceed by tin—tin bond cleavage, since tin—carbo cleavage in tetramethyltin and trimethyl-t-butyltin are considerably slower (Table 3), and dimethylmercury is not formed in sufficiently high yields. (The dimethylmercury yield is not reduced by its reaction with trimethyltin chloride to yield tetramethyltin and methylmercuric chloride since this reaction in fact occurs in the reverse direction. As can be seen from the data of Table 3 this reverse reaction is too slow to be the source of dimethylmercury.)

Several mechanisms may be excluded on the basis of the absence of species of the type $RHgCH_3$ in the product. When the reagent is CD_3HgCl the dimethylmercury product is exclusively $(CD_3)_2Hg$, demonstrating that there is no detectable Sn—C cleavage by this reagent.

It might be supposed that dimethylmercury could arise through reaction 15.

$$2RHgX \underset{-15}{\overset{15}{\rightleftharpoons}} R_2Hg + HgX_2 \qquad (15)$$

with the mercuric halide formed reacting rapidly with hexamethylditin as in eqn. 12. However this provides no path for the formation of tetramethyltin. Furthermore the kinetic form for both methyl and vinylmercuric chloride does not correspond to that expected if reaction 15 were rate controlling nor if it were a pre-equilibrium step, (cf. eqn. 8 of Results section), and bis(*trans*-2-chloro vinyl)mercury has no rate depressing effect.

TABLE 4

DIMETHYLMERCURY—MERCURIC HALIDE REACTIONS[a, b]

$$2\,CH_3HgX \underset{-15}{\overset{15}{\rightleftarrows}} (CH_3)_2Hg + HgX_2$$

X	k_{-15} ($M^{-1}s^{-1}$)	K^{-1}	k_{15} ($M^{-1}s^{-1}$)
Cl	1.05	3.5×10^{11}	$\approx 3 \times 10^{-12}$
Br	0.30	2.5×10^{9}	$\approx 1.2 \times 10^{-10}$
I	0.05	3.4×10^{5}	$\approx 1.5 \times 10^{-7}$

[a] In methanol; 30°. [b] See refs. 18 and 19.

An estimate of the rate of reaction 15 can be made from the measured rates of reaction —15 (methanol, 36°) [18] and the estimated equilibrium constants [19]. The results summarised in Table 4 demonstrate that reaction 15 can play no significant role. A further estimate of the rate of step 15 in the case of methylmercuric bromide can be obtained as follows. For ethanol solutions at 25° mercuric bromide is ca. 10^4 times more reactive than 2-butylmercuric bromide towards di-2-butylmercury [20, 21] (Table 3 indicates a similar reactivity differential between mercuric chloride and methylmercuric chloride). Since mercuric bromide reacts with methylmercuric bromide in ethanol at 20° with a rate constant [22] of ca. $2 \times 10^{-7}\ M^{-1}\ s^{-1}$, one may estimate $k_{15} \approx 2 \times 10^{-11}\ M^{-1}\ s^{-1}$. Although reaction 15 is unimportant for the halides it is possible that it is the rate step for methylmercuric cyanide.

Tetramethyltin is formed by the trimethyltin chloride catalysed decomposition of hexamethylditin [10]. However the rate of this reaction under present conditions would not yield significant quantities until the observed reaction is ca. 90% complete whereas this product is in evidence throughout.

The variation in the ratio of tetramethyltin to dimethylmercury during reaction and the almost exclusive formation of the latter when the methylmercuric chloride concentration is maintained high throughout the reaction are consistent with the two suggested modes of destruction of the trimethylstannyl mercurial (reactions 14b and 14c). This aspect of the reaction is considered in detail in the following paper [23].

Vinylmercuric chloride and *trans*-chlorovinylmercuric chloride, k_{obs} 6.3×10^{-3} and $1.6 \times 10^{-2}\ M^{-1}\ s^{-1}$ respectively, are rather more reactive than methylmercuric chloride, presumably since a more electronegative group is bonded to the electrophilic mercury. They yield products corresponding to a small k_b/k_c ratio in eqn. 14. It cannot be inferred, however, that path b is not followed, since the product in the former case, trimethylvinyltin, would undergo reaction with vinylmercuric chloride, k $0.11 \times 10^{-1}\ M^{-1}\ s^{-1}$, at a rate nearly twenty times its rate of formation. Phenylmercuric acetate appears to follow the same behaviour as the vinyl reagents.

Our results demonstrate that reaction 2 is rather more complex than previously described and that it will not in general provide a useful method for the preparation of R_3SnR' species unless the R'—Sn bond is not susceptible to cleavage by R'HgX. This clearly precludes the use of the more reactive organomercuric salts, e.g. acetates, and the introduction of reactive R′ groups such as vinyl and aryl, although the formation of nitrophenyltrimethyltins may be possible. It seems likely that in the previous use of reaction 2, i.e. 150° for 3 h, $R'HgCl$ was rapidly converted to R'_2Hg without R_3SnR' formation. The R_3SnR' product obtained could have arisen subsequently from reaction 3 employing unreacted R_6Sn_2.

Reaction 3 remains the best approach to R_3SnR' where the Grignard method is inapplicable provided that thermal decomposition of the product is not serious. It is certainly of a different mechanistic type from reaction 1 and 2 and may proceed by a homolytic pathway, for example:

$$R_6Sn_2 \rightleftharpoons 2R_3Sn\cdot$$

$$R_3Sn\cdot + R'_2Hg \rightarrow R_3SnR' + R'Hg\cdot$$

$$R'Hg\cdot \rightarrow R'\cdot + Hg$$

$$R'\cdot + R_6Sn_2 \rightarrow R_3SnR' + R_3Sn\cdot$$

This possibility is being examined as part of a study of the thermal decomposition of hexamethylditin and hexamethyldilead.

Acknowledgements

These investigations were supported by a grant from the Australian Research Grants Committee.

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