

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIFORNIA]

## Some Effects of Boron Lewis Acids upon Methyltin Compounds<sup>1</sup>

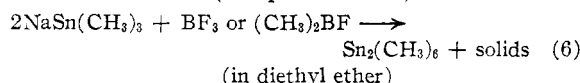
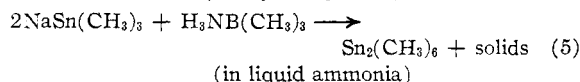
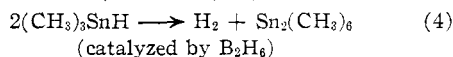
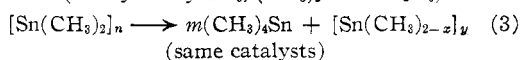
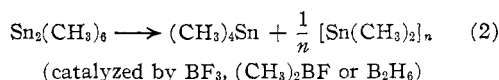
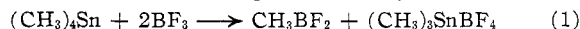
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The salt  $\text{NaSn}(\text{CH}_3)_3$  in liquid ammonia reacts with  $\text{H}_3\text{NB}(\text{CH}_3)_3$  in such a manner that yields of  $\text{Sn}_2(\text{CH}_3)_6$  above 90% are obtained upon warming to room temperature. However, when  $\text{NaSn}(\text{CH}_3)_3$  reacts with  $\text{BF}_3$  or  $(\text{CH}_3)_2\text{BF}$  in diethyl ether, the yields of  $\text{Sn}_2(\text{CH}_3)_6$  are far smaller. The main reason is found in the catalytic disproportionation of  $\text{Sn}_2(\text{CH}_3)_6$  by these Lewis acids, producing methyltin polymers and tetramethyltin; then  $\text{BF}_3$  reacts with the latter to make  $\text{CH}_3\text{BF}_2$  and the new compound  $(\text{CH}_3)_3\text{SnBF}_4$  (m.p.  $89^\circ$ ; dissociable with liberation of  $\text{BF}_3$ ). The decomposition of  $(\text{CH}_3)_3\text{SnH}$  to  $\text{H}_2$  and  $\text{Sn}_2(\text{CH}_3)_6$  is catalyzed by diborane, which also is an effective catalyst for the disproportionation of  $\text{Sn}_2(\text{CH}_3)_6$ .

Recent studies have indicated that alkyltin compounds are reactive toward Lewis acids. For example,  $\text{R}_4\text{Sn}$  compounds react with tin tetrahalides to make alkyltin halides<sup>2</sup>; or boron trichloride exchanges chloride for a  $\text{C}_2\text{H}_5$  or  $\text{C}_2\text{F}_5$  group from tin.<sup>3</sup> Similarly,  $\text{BF}_3$  attacks  $(\text{CH}_3)_3\text{SnCF}_3$  to make  $(\text{CH}_3)_3\text{Sn}(\text{CF}_3\text{BF}_3)$ , leading to salts of the  $\text{CF}_3\text{BF}_3^-$  ion.<sup>4</sup>

The results of the present study are summarized



The work actually began with reactions (5) and (6), which represented attempts to form a covalent Sn-B bond. It was assumed that the lone-pair electrons on tin would have enough base strength to form such a bond (at least as the first of a series of reactions), but we found no way to demonstrate this. The solid by-product of (5) was far from simple, behaving like a source of methide ion and apparently including B-B bonded polymers. The reason for a low yield of  $\text{Sn}_2(\text{CH}_3)_6$  from (6) was found through experiments leading to equations (1) through (4).

Reaction (1) evidently is related to the addition of  $\text{BF}_3$  to  $(\text{CH}_3)_3\text{SnCF}_3$ <sup>4</sup> but ends differently because  $\text{CH}_3\text{BF}_2$  is a weaker Lewis acid than  $\text{BF}_3$ ,<sup>5</sup> whereas  $\text{CF}_3\text{BF}_2$  is stronger.<sup>6</sup> The resulting  $(\text{CH}_3)_3\text{SnBF}_4$

melts near  $89^\circ$  in a sealed tube; or *in vacuo* at  $100^\circ$  it forms a white sublimate with loss of  $\text{BF}_3$  and a sharp decrease of equilibrium pressure. It reacts with diethyl ether to form two liquid phases; and its high solubility in water doubtless also includes a chemical reaction.

The low m.p. of  $(\text{CH}_3)_3\text{SnBF}_4$  is an argument against the ionic structure  $(\text{CH}_3)_3\text{Sn}^+\text{BF}_4^-$ ; however, we have no basis for choosing among structures having one, two or three Sn-F-B bridge bonds. Some relation to the very unstable  $(\text{CH}_3)_3\text{SiBF}_4$ <sup>7</sup> might be considered.

Reactions (2) and (3) describe the metastability of hexamethyldistannane relative to tetramethyltin and methyltin polymers. Some of the solids were white, while others had the yellow color of the long-known dimethyltin polymer,<sup>8</sup> suggesting that reaction (2) occurred even though the stoichiometry would imply much destruction of this polymer by reactions described by equation (3). In one experiment, indeed, the solid product contained only 0.7  $\text{CH}_3$  per tin atom. With  $\text{BF}_3$  as a catalyst, of course, reaction (1) also was extensive.

Reaction (4) represents an attempt to make the hypothetical  $(\text{CH}_3)_3\text{SnBH}_4$ . Again the equation is idealized, for the actual results were complicated by extensive occurrence of reaction (2).

### Experimental Part

The experimental work here reported was performed by means of a high-vacuum manifold, permitting quantitative monitoring of reactions involving volatile substances. Samples of well purified reactants and products were either measured as gases or weighed in detachable stop-cock tubes. The volatile products all were known substances, which could be identified by their molecular weights and other physical properties.

**Reaction (1): Trimethyltin Fluoborate.**—Measured samples of  $(\text{CH}_3)_4\text{Sn}$  and  $\text{BF}_3$  were sealed in glass tubes and brought to reaction under the conditions indicated in Table I. The product  $\text{CH}_3\text{BF}_2$  showed the vapor tensions 69.5 mm. at  $-97.4^\circ$  and 286.9 mm. at  $-78.5^\circ$  (calcd., 70.1 and 287.2 mm.)<sup>9</sup> and mol. wt. 62.8 (calcd., 63.8). The non-volatile residue of expt. 1, presumably a mixture of  $(\text{CH}_3)_3\text{SnF}$  and  $(\text{CH}_3)_3\text{SnBF}_4$ , melted at  $90-92^\circ$ ; that from expt. 4 at  $82.0-89.4^\circ$  under 20 mm. pressure of  $\text{BF}_3$ . Another preparation (not listed in Table I) melted in a small sealed tube at  $88.9-89.4^\circ$ . Pressure measurements for the dissociation  $(\text{CH}_3)_3\text{SnBF}_4 \rightarrow (\text{CH}_3)_3\text{SnF} + \text{BF}_3$  were complicated by the changing composition of the liquid phase as  $\text{BF}_3$  came off to register higher equilibrium pressures at higher temperatures. The effect was to diminish the slope of the  $\log P$  vs.  $1/T$

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(1) This research was supported by the Office of Naval Research under Contract Nonr-228(13). Much of the work was described in the M.Sc. Thesis by John R. Spielman, University of Southern California Libraries, 1958. Reproduction is permitted for any purpose of the United States Government.

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TABLE I  
 THE  $(\text{CH}_3)_3\text{Sn}-\text{BF}_3$  REACTION

Expt. no.	Reactants (mmole)		Time (hr.)	Temp. ( $^{\circ}\text{C}.$ )	Volatile components (mmole)			Sn:B Ratio in residue
	$(\text{CH}_3)_3\text{Sn}$	$\text{BF}_3$			$(\text{CH}_3)_3\text{Sn}$	$\text{BF}_3$	$\text{CH}_3\text{BF}_2$	
1	0.693	0.803	2	100	0.194	Nil	0.473	1.51
2	(Residue of No. 1)		2	100	Nil	0.556	Nil	0.99
3	0.586	1.260	16	20	0.322	0.732	0.264	1.00
4	0.582	1.283	2	100	0.168	0.451	0.401	0.98

TABLE II

CATALYTIC DISPROPORTIONATION OF $\text{Sn}_2(\text{CH}_3)_6$					Volatile components (mmoles)
Expt. no.	Starting materials (mmoles)	Temp. ( $^{\circ}\text{C}.$ )	Time (hr.)		
1	$\text{Sn}_2(\text{CH}_3)_6$ 0.113	100	38	$\text{Sn}_2(\text{CH}_3)_6$	0.111
2	$\text{Sn}_2(\text{CH}_3)_6$ 1.096	20	24	$\text{Sn}(\text{CH}_3)_4$	0.780
	$\text{BF}_3$ 2.699			$\text{CH}_3\text{BF}_2$	0.756
3	$\text{Sn}_2(\text{CH}_3)_6$ 0.122	100	36	$\text{BF}_3$	1.118
	$(\text{CH}_3)_2\text{BF}$ .131			$\text{Sn}_2(\text{CH}_3)_6$	0.020
				$\text{Sn}(\text{CH}_3)_4$	.124
4	$\text{Sn}_2(\text{CH}_3)_6$ .330	100	1	$(\text{CH}_3)_2\text{BF}$	.131
	$\text{B}_2\text{H}_6$ .565			$\text{Sn}(\text{CH}_3)_4$	.459
				$\text{B}_2\text{H}_6$	.491
				$\text{H}_2$	.062

curve, giving an absurdly low  $\Delta H$  value, when the vapor-phase volume was not small relative to the size of the sample. However, in a relatively small tensimeter, a sublimate having the composition  $(\text{CH}_3)_3\text{SnF} \cdot 0.80\text{BF}_3$  was measured in the range 2.8 mm. at  $102^{\circ}$  to 33 mm. at  $163^{\circ}$ , with results conforming very well to the equation  $\log P_{\text{mm.}} = 8.1028 - 2870/T$ . From this,  $\Delta H = 13.1$  kcal./mole and  $\Delta H/T_{760} = 23.8$  cal./deg. mole. These values could represent the detachment and vaporization of the single component  $\text{BF}_3$  from the liquid phase but would be too low if any  $(\text{CH}_3)_3\text{SnF}$  also were being vaporized.

It appears from the results of Table I that the equation  $(\text{CH}_3)_3\text{Sn} + \text{BF}_3 \rightarrow \text{CH}_3\text{BF}_2 + (\text{CH}_3)_3\text{SnBF}_4$  is virtually exact in terms of the reactants consumed, provided that enough  $\text{BF}_3$  is present.

**Reaction (2): Disproportionation of the Distannane.**—The air-sensitive hexamethyldistannane was prepared by the action of sodium on trimethyltin chloride in liquid ammonia<sup>10,11</sup> and purified by high-vacuum sublimation; m.p.  $23.5^{\circ}$  (known value);<sup>12</sup> vapor tension 1.0 mm. at  $25^{\circ}$ . The conditions and results of the sealed-tube experiments on its catalytic disproportionation are shown in Table II.

Experiment 1 showed that the disproportionation of  $\text{Sn}_2(\text{CH}_3)_6$  does not occur readily without a catalyst. Experiment 2 may be understood in terms of equation (2) if it is assumed that much of the yellow dimethyltin polymer disproportionated to a far less methylated tin material and tetramethyltin, with the latter reacting further according to equation (1). Thus the final solid residue, still showing a yellow color indicative of the dimethyltin polymer and containing 1.412 mmole of Sn, 2.700 mmole of  $\text{CH}_3$  groups, 0.825 mmole of B and 3.231 mmole of F, could be interpreted as 0.825 mmole of  $(\text{CH}_3)_3\text{SnBF}_4$  with a methyltin material written empirically as  $[\text{Sn}_2(\text{CH}_3)_2]_x$ .

In Expt. 3 the catalyst evidently was less effective for reaction (2), since some  $\text{Sn}_2(\text{CH}_3)_6$  survived; however, it seems that some process of type (3) was important, for the solid product, empirically written as  $[\text{Sn}(\text{CH}_3)_{1.46}]_x$  was white and so could not have included much dimethyltin polymer. Here there was no boron compound capable of reacting in the manner of equation (1), so that the yield of tetramethyltin was higher than demanded by equation (2), having been derived partly from reaction (3) and recovered without further reaction.

Experiment 4 showed that diborane is a relatively effective catalyst, for it destroyed the whole sample of  $\text{Sn}_2(\text{CH}_3)_6$  in one hour at  $100^{\circ}$  and left a methyltin residue relatively poor in methyl groups. The formation of hydrogen corresponded to the normal decomposition of diborane, the loss of which should not be attributed to any net contribution of material

to the main methyltin reactions; its function was purely catalytic.

**Reaction (4): Condensation of Trimethylstannane.**—A 1.129 mmole sample of  $(\text{CH}_3)_3\text{SnH}$  was heated with 1.112 mmole of  $\text{B}_2\text{H}_6$  in a sealed tube at  $70^{\circ}$  for 1.5 hr., after which the  $\text{B}_2\text{H}_6$  was wholly recovered (measured, 1.112 mmole). The recovery of 0.603 mmole of  $(\text{CH}_3)_3\text{SnH}$  meant that 0.526 mmole had been used up. Then the formation of  $\text{H}_2$  was nearly in accord with equation (4): found, 0.255 mmole; calcd., 0.263. The yield of  $\text{Sn}_2(\text{CH}_3)_6$  was 0.083 mmole, or 32% of the calcd. 0.263; the rest was accountable by reactions (2) and (3), forming 0.155 mmole of  $(\text{CH}_3)_3\text{Sn}$  and a non-volatile yellow residue having the empirical formula  $[\text{Sn}(\text{CH}_3)_{2.24}]_x$ . This would correspond to an open-chain polymer averaging seven  $\text{Sn}(\text{CH}_3)_2$  units per two  $(\text{CH}_3)_3\text{Sn}$  end-groups. Thus under milder conditions than in Expt. 4 of Table II, reaction (2) was extensive while reaction (3) occurred only to a small extent if at all.

**Reaction (5).**—The salt  $\text{NaSn}(\text{CH}_3)_3$  was made by treating  $(\text{CH}_3)_3\text{SnCl}$  with sodium in liquid ammonia.<sup>10,13</sup> A solution containing 2.85 mmole of this salt with 3.90 mmole of  $\text{H}_3\text{NB}(\text{CH}_3)_3$  was warmed from  $-77$  to  $-35^{\circ}$  without apparent change; but after evaporation of the liquid ammonia and further warming to room temperature, 0.4 mmole of  $\text{CH}_4$  and 1.18 mmole of  $\text{Sn}_2(\text{CH}_3)_6$  (0.8 mm. at  $23^{\circ}$ ; m.p.  $23.5^{\circ}$ ; density 1.55 at  $25^{\circ}$  vs. known 1.57)<sup>10</sup> were removed *in vacuo*. The residue was warmed slowly to  $90^{\circ}$ , bringing the total  $\text{CH}_4$  to 4.2 mmole and the final yield of  $\text{Sn}_2(\text{CH}_3)_6$  to 1.30 mmole, representing 91% of the original  $\text{Sn}(\text{CH}_3)_3$  groups. Thus the residue contained material equivalent to 0.25 mmole of  $\text{NaSn}(\text{CH}_3)_3$ , along with 3.90 mmole of boron, 7.5 mmole of  $\text{CH}_3$  groups and 2.60 mmole of sodium, presumably in the form of amide to which the methylated boron material was attached. This residue was treated with as much  $\text{HCl}$  as would react at room temperature, liberating 0.15 mmole of  $(\text{CH}_3)_3\text{SnCl}$ , 0.38 mmole of  $\text{B}(\text{CH}_3)_3$ , 0.50 mmole of  $\text{CH}_4$  and 0.59 mmole of  $\text{H}_2$ . Thus it seems that the boron had several forms: aside from the indicated complex of  $\text{B}(\text{CH}_3)_3$  there must have been some methidic B- $\text{CH}_3$  material (doubtless enhanced by amide complex-formation), and probably there were some B-B bonds whose  $\text{HCl}$ -cleavage would account for the formation of  $\text{H}_2$ . Yet another probable component would be a relatively inert and highly condensed methylboron polymer.

**Reaction (6).**—For the experiments in ether solution, the  $\text{NaSn}(\text{CH}_3)_3$  was made from tetramethyltin with sodium in liquid ammonia.<sup>10</sup> The ammonia solution was filtered and most of the ammonia was removed by high-vacuum sublimation, with warming to  $-25^{\circ}$ . Then the product was dissolved in diethyl ether at that temperature and treated with  $\text{BF}_3$  or  $(\text{CH}_3)_2\text{BF}$ ,<sup>14</sup> with warming to  $0^{\circ}$ . When the ratio of  $\text{BF}_3$  to  $\text{NaSn}(\text{CH}_3)_3$  was close to 2:1, the reaction gave a white precipitate and a yellow solution, but no appreciable yield of  $\text{Sn}_2(\text{CH}_3)_6$ , evidently because reaction (2) destroyed any of it which might have been formed. With a 1:1 ratio, however,  $\text{Sn}_2(\text{CH}_3)_6$  was produced in a 19.7% yield. This result may represent a genuinely effective action of  $\text{BF}_3$  for conversion of  $\text{NaSn}(\text{CH}_3)_3$  to  $\text{Sn}_2(\text{CH}_3)_6$ , for a dry sample of  $\text{NaSn}(\text{CH}_3)_3$  decomposed at room temperature to give only a 10% yield of  $\text{Sn}_2(\text{CH}_3)_6$ . However, the less catalytically destructive  $(\text{CH}_3)_2\text{BF}$  led to higher yields of  $\text{Sn}_2(\text{CH}_3)_6$ . For example, 1.53 mmole of  $\text{NaSn}(\text{CH}_3)_3$  and 0.67 mmole of  $(\text{CH}_3)_2\text{BF}$  produced 0.32 mmole of  $\text{Sn}_2(\text{CH}_3)_6$ , representing 42% of the originally-present  $\text{Sn}(\text{CH}_3)_3$  groups.

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