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AN INVESTIGATION OF METHYLTIN-LITHIUM COMPOUNDS PREPARATION AND PROPERTIES OF TRIS(TRIMETHYLSTANNYL)-STANNYLLITHIUM TRIS(TETRAHYDROFURAN)*

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INTRODUCTION

The preparations and properties of a number of trialkyl- and triarylstannyllithium compounds have been described in the literature[1]. Although these have found use as synthetic intermediates, little effort has been directed toward understanding their structures. The possibility that a compound of the form R_3SnLi might be involved in an equilibrium of the form

$$R_3SnLi \rightleftharpoons R_2Sn + RLi \qquad (1)$$

has been considered. Gilman and Rosenberg failed to find evidence for such an equilibrium in the case of triphenylstannyllithium in ether[2]. Coates, Blake, and Tate on the other hand[3], observed product distributions in the reactions of tributylstannyllithium which suggested that the equilibrium might be important. In any case, it is well known that tin–carbon and tin–tin bonds are much more labile to rearrangement than the analogous silicon systems which have been extensively studied.

The nature of the simple organolithium compounds has become much better understood during the past few years. It is now well recognized that they are associated, even in quite polar solvents, through formation of alkyl group bridge bonds[4,5]. It was of interest to determine if the alkylstannyllithium compounds possess similar structural characteristics. If these compounds were found to be associated as the simple alkyllithium compounds, it would represent an extension of what is sometimes referred to as "electron deficient" bonding to an element other than carbon or hydrogen.

RESULTS AND DISCUSSION

Trimethylstannyllithium (I) in THF can be prepared by one of three different methods, with essentially the same results in each case. We relied most heavily on the preparation from hexamethylditin, to avoid the complicating effects of lithium halide. In THF (I) is a very stable substance. A sample in a sealed NMR tube was left at room temperature for a period of several months with no evidence of decomposition. Neither does there appear to be a marked photochemical sensitivity. The very low

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coupling constant of 5.2 cps between the methyl group protons and the two tin nuclides of spin $\frac{1}{2}$, ^{117}Sn and ^{119}Sn, (Table 1) is indicative of a trimethyltin group bonded to a strongly electron-releasing moiety[6]. It would appear that some slight variations in

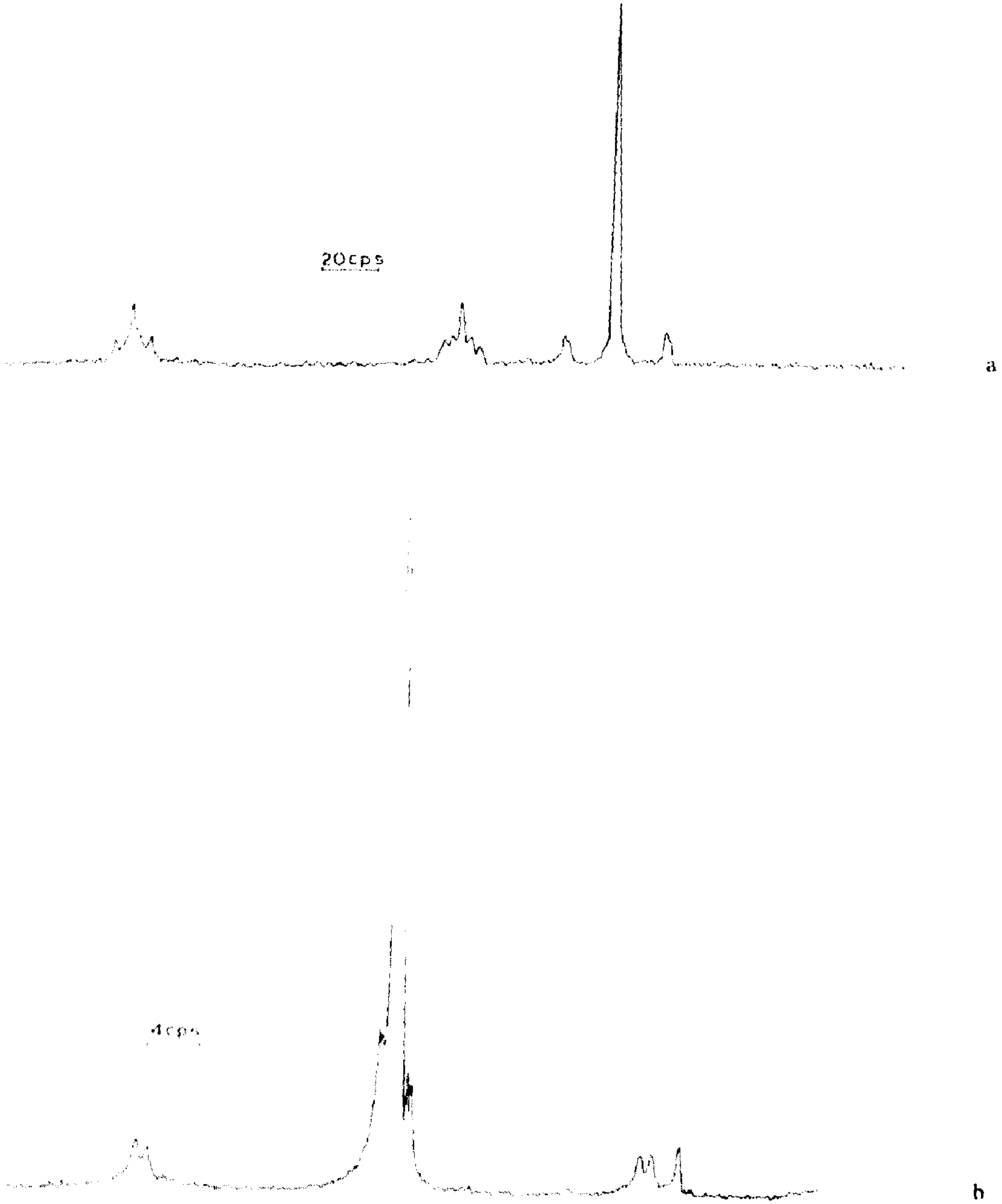


Fig. 1. (a) Proton NMR spectrum of a benzene solution of recrystallized $[(CH_3)_3Sn]_3SnLi\cdot(OC_4H_8)_3$. For chemical shift data, see Table 1 and text. (b) Proton NMR spectrum of the methyl group resonance ($\tau = 9.40$) in a benzene extract of $[(CH_3)_3Sn]_3SnLi\cdot(OC_4H_8)_3$. The small absorption upfield from the tin–proton coupling doublet is due to an unidentified impurity.

this coupling may arise from the presence or absence of ion pairing, since the coupling constant is increased to 7.5 cps when lithium halide is present, but the general indication is of an ionic bonding, $(CH_3)_3Sn^-Li^+$.

A mixture of (I) and methyllithium in THF exhibits two proton resonances in the NMR, indicating a slow exchange of methyl groups between the two kinds of sites. This means that equilibrium (1), if it occurs at all, is slow on the NMR time scale.

Attempts were made to prepare dimethylstannyldilithium by reaction of lithium metal with dimethyltin dichloride in THF. The reaction was attempted at various temperatures and with various forms of lithium metal. In no case was a substance produced which could be identified as the desired compound. The most common result was the formation of trimethylstannyllithium, I, which could be quite unambiguously identified by its proton and ^{7}Li NMR spectra. This result shows quite clearly the lability of tin–carbon and tin–halogen bonds.

Attempts were made to isolate (I) either as a pure substance or as a complex with THF for further study. All attempts to do this, however, have led to decomposition to the previously unreported compound, tris(trimethylstannyl)stannyllithium tris(tetrahydrofuran), $[(CH_3)_3Sn]_3SnLi\cdot(OC_4H_8)_3$, (II). It is quite remarkable that although (I) is a stable compound in THF, attempts to remove solvent, even at −78°, lead immediately to decomposition with (II) as the major identified product. Tetramethyltin and an intensely reactive solid material of high lithium content are the other components of a mixture resulting from solvent removal. The tetramethyltin is removed and trapped out along with solvent.

(II) can be extracted into benzene from the solid matrix after THF removal. Concentration of this benzene solution, followed by addition of pentane and chilling, results in formation of straw-colored crystals of (II).

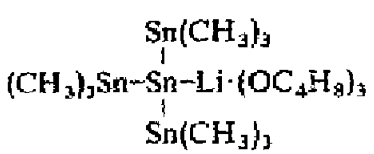
The proton NMR spectrum of (II) in benzene is shown in Fig. 1. The relevant chemical shifts and coupling constants are listed in Table 1. It is quite evident that (II) is not the same compound as (I). Redissolving of (II) into THF results in a spectrum very similar to that in Fig. 1, except that the sidebands close to the central absorption at τ = 10.0 are not resolved. The spectra also reveal the presence of THF molecules. From the integrated areas, there is found to be one THF molecule per nine protons in the central absorption. This result was repeated on a number of samples. Assuming that the compound contains trimethyltin groups, there is then one THF molecule per $(CH_3)_3Sn$ group. The NMR spectral evidence is consistent with the structure

TABLE 1

^{1}H AND ^{7}Li NMR DATA FOR TRIMETHYLSTANNYLLITHIUM AND TRIS(TRIMETHYLSTANNYL)STANNYLLITHIUM TRIS(TETRAHYDROFURAN)

Compound	*Solvent*	$J(^{117,119}Sn\text{–}C\text{–}H)^a$	$J(^{117,119}Sn\text{–}Sn\text{–}C\text{–}H)^a$	$\tau(^1H)^b$	$\delta(^7Li)^b$
$(CH_3)_3SnLi^c$	THF	7.5		10.40	0.21
$(CH_3)_3SnLi^d$	THF	5.2		10.40	0.21
$[(CH_3)_3Sn]_3SnLi\cdot 3\,THF$	C_6H_6	37, 39	2.3	9.40	0.64
$[(CH_3)_3Sn]_3SnLi\cdot 3\,THF$	THF	33, 35		10.04	0.99

[a] In cps. [b] In ppm. [c] Prepared by Methods A or B. [d] Prepared by Method C.



$$\mathrm{(CH_3)_3Sn{-}}\underset{\underset{\mathrm{Sn(CH_3)_3}}{|}}{\overset{\overset{\mathrm{Sn(CH_3)_3}}{|}}{\mathrm{Sn}}}\mathrm{{-}Li\cdot(OC_4H_8)_3}$$

(II)

In an attempt to further characterize the new substance, both tin and lithium analyses were carried out. The results for tin are not as precise as one might hope for; (II) is an extremely reactive substance which decomposes immediately upon contact with air and which is violently reactive with acidic water. This made the gravimetric estimation of tin quite difficult, but the flame photometric analysis for lithium could be effected without difficulty. The empirical formula for the new substance seems quite unambiguously determined by the combined analytical and NMR data. The structure of the compound is revealed in the NMR spectrum. One expects that there should be a single methyl group resonance, with possibly two characteristic coupling constants. There should be a 117/119 doublet corresponding to coupling of the protons to the near tin atom. By analogy with the results for other methyltin groups bonded to another metal atom which should be relatively electron-releasing[7,8], the coupling constants might be expected to be less than 40 cps. The observed values of 33 and 35 cps for THF solutions of (II) are quite reasonable. Coupling of the methyl protons to the central tin should be quite small. Since the central tin atom carries the lithium atom it contains a substantial negative charge. We have already seen that coupling of protons to tin in $(CH_3)_3Sn^-$ is small; by analogy the coupling in $[(CH_3)_3Sn]_3Sn^-$ should also be small. The observed value is 2.3 cps. The magnitude of the scalar spin–spin coupling is often discussed in terms of the fractional *s* character in the bonds employed by the interacting centers[9]. In this terminology the fractional *s* character in the orbital containing an unshared electron pair is high, and correspondingly low in the bonds to the other atoms.

(II) is not stable for long in any solvent which we have used other than THF. Benzene solutions are subject to rather rapid decomposition at room temperature. It was not possible, therefore, to obtain accurate molecular weight data from freezing point lowerings. (II) was further characterized by ^{7}Li NMR spectra, mass spectra, and by infrared spectra of nujol mulls of the crystals (see Experimental). Attempts to form characteristic derivatives with (II) were largely unsuccessful. The compound is subject to such facile rearrangements that a variety of products resulted in every case. Some evidence of the lability of the substance is to be found in the behavior of THF solutions made up from recrystallized (II) and freshly prepared (I). At room temperature the proton NMR spectrum consists of the solvent peaks plus a broad absorption. At lower temperatures (−30°) the spectrum consists of the absorptions characteristic of (I) and (II). There is apparently a rapid exchange of trimethyltin groups in this system at room temperature. The exchange process probably consists of a nucleophilic attack on (II) by $(CH_3)_3Sn^-$.

Attempts to form derivatives of (II) with trimethylsilyl chloride and triphenyltin chloride were unsuccessful. Reaction with methyl bromide at 0° led to a complex mixture which was not separated. From the proton NMR spectrum, however, it appeared that the expected product, tris(trimethylstannyl)methyltin, was present in low yield.

Reaction of Br_2 with (II) leads to formation of trimethyltin bromide as the only identifiable product; reaction with $Mn(CO)_5Br$ yielded $Mn(CO)_5Sn(CH_3)_3$.

Gilman and Cartledge[9] have recently reported on the properties of the analogous phenyl compound, $[(C_6H_5)_3Sn]_3SnLi$. Derivatization reactions in this case also proved to be difficult. The compound $[(C_6H_5)_3Sn]_3SnCH_3$ was obtained in low yields with trimethylphosphate and methyl iodide; hexaphenylditin is the principal product. The general chemical behavior of the phenyl compound in THF solution indicates the $[(C_6H_5)_3Sn]_3Sn^-$ moiety is more stable than the corresponding methyl species.

In the absence of really satisfactory identification of a derivative of (II) which would prove its structure, it was of interest to see whether the compound might be prepared by another route than decomposition of (I). A THF solution of (I) was allowed to react with anhydrous $SnCl_2$. Aside from some hexamethylditin, the sole product of the reaction, identified by the NMR spectrum, was (II).

From the observation that three molecules of THF are held very tenaciously and can be removed only by decomposing (II), it would appear that the compound is quite ionic in character. It is not clear just why (II) forms so readily from (I) as solvent is removed. The decomposition probably proceeds through formation of trimethyltin radicals. A series of consecutive reactions involving extraction of methyl radicals to form tetramethyltin, and coupling of tin-containing radicals accounts for the observed products, but there is no evidence as yet regarding mechanism.

It should perhaps be remarked that the decomposition does not appear to occur in solution, but in the solid slurry which results from removal of solvent. Attempts to form (II) from (I) in THF solution in a photochemical raction have not been successful, but this possibility has not been exhausted by our preliminary efforts.

The nature of the bonding in (II) is not entirely clear at this point. From the low values for the coupling constants between the methyl protons and the near tin atom it would appear that the trimethyltin groups carry a moderately high charge. This may result from delocalization of the charge on the central tin through π bonding[10]. A facile transfer of charge to the trimethyltin groups, as suggested by a π bonding scheme, would help to account for the ease of exchange of trimethyltin groups with (I). It may be that even in solutions of (II) alone in THF there is a rapid intermolecular exchange of trimethyltin groups. This would be consistent with the absence of the small coupling of protons to the central tin which is evident in benzene solutions of (II), but apparently absent in the THF solutions. At the same time there would remain, of course, the coupling to the tin within the $(CH_3)_3Sn$ group.

Experiments similar to those described here were conducted earlier by G. L. Morgan in these laboratories[11], with diethyl ether as solvent. Similar behavior was noted in most respects. The proton resonance spectrum of a benzene extract after solvent removal showed the presence of ether in the ratio of one ether to each trimethyltin group. The central absorption occurs at $\tau = 9.46$, with coupling constants of 38.3, 39.9 and 3.2 cps in benzene.

The ether complex, $[(CH_3)_3Sn]_3SnLi \cdot [O(C_2H_5)_2]_3$, is considerably less stable than the THF complex. Decomposition in benzene leads to formation of tetramethyltin and a deeply colored solid residue. There is indication in the slightly higher coupling constants for the ether complex that the central tin atom carries less negative charge. There seems to be at least a small degree of covalent interaction between lithium and the tin, which varies with base strength of the solvating molecules. These results suggest that more stable complexes of the new substance might be formed with bases such as tetramethylethylenediamine, or with polyethers.

EXPERIMENTAL

Materials

Trimethyltin chloride was generously furnished by M and T Chemicals, Inc., Rahway, New Jersey. Tetrahydrofuran (THF) Analytical Reagent Grade, was refluxed over KOH and iron for twelve hours or more, distilled onto lithium aluminum hydride, and then distilled under an argon atmosphere and stored over sodium wire. Analytical grade benzene was filtered through a long column of freshly activated silica gel and stored over sodium wire under an argon atmosphere. Pentane was stored over sodium wire until used. The lithium employed was low sodium variety, obtained from Lithium Corporation of America. Stannous chloride was rendered anhydrous by reacting 75 g of the dihydrate with 75 ml acetic anhydride[12]. The white slurry resulting from the reaction was filtered on a Büchner funnel, and washed with several portions of anhydrous ether. The dry powder was then recrystallized from THF and stored in a vacuum desiccator until used.

Dimethyltin dichloride, obtained from M and T Chemicals, Inc., was recrystallized from benzene, then petroleum ether, then benzene again. Hexamethylditin was sometimes purchased from commercial sources, but more often synthesized from trimethyltin chloride by a modification of the procedure of Kraus and Sessions[13].

Methyllithium was prepared from reaction of methyl chloride and lithium metal at 0° in the solvent of choice, usually THF. The NMR spectrum of the THF solutions of methyllithium exhibits a proton resonance at $\tau = 12.05$.

Instrumental methods

Proton NMR spectra were obtained on a Varian Associates model A-60 spectrometer. ^{7}Li spectra were obtained on a Varian model DP-60, at a frequency of 23.3 Mc. All air-sensitive samples were sealed into sample tubes under high vacuum after thorough degassing. Proton chemical shift values were related to tetramethylsilane through the measured chemical shifts from this standard for each solvent. The ^{7}Li chemical shifts were measured relative to the signal from an aqueous LiBr solution inserted as a capillary.

IR spectra were obtained on a Beckman IR-5A with cesium bromide optics. Mass spectra were obtained on an Atlas model CH-4, using the direct sample inlet, and sample heating.

Lithium analysis was performed by flame photometry on a Beckman DUR, using an oxygen-hydrogen flame and an RCA No. 6217 photometer head with an S.10 response.

All operations involving air-sensitive materials were carried out in glass apparatus under argon, or in an inert atmosphere glove box with argon atmosphere.

Preparation of $(CH_3)_3SnLi$ (I) in THF

Three methods were employed in preparation of (I).

Method A involves the direct reaction of methyllithium with anhydrous tin(II) chloride in THF. On the basis of a large number of attempts, with various reaction conditions, we conclude that the reaction leads to reasonable yields of (I) only when conducted at dry ice-acetone bath temperature. The reaction was conducted in all cases by adding a THF solution of methyllithium to $SnCl_2$ in THF. As the addition progressed the solution turned a deep red in color. The reaction solution was allowed to stir for 11 h, and then left standing at dry ice-acetone bath temperature for an additional 8 h. The solution was warmed to room temperature and filtered. The deep red filtrate showed the presence of (I), identified by the NMR spectrum. Since a slight excess of methyllithium was usually employed, this substance also was apparent in the NMR spectrum, along with a small amount of an unidentified substance which gave a resonance at $\tau = 9.97$. When the reaction was conducted at room temperature or at 0°, the products consisted of only methyltin polymeric species.

Method B consisted in reaction of trimethyltin chloride with lithium metal, as described by Tamborski and co-workers[14]. Identification of (I) was effected by observation of the NMR spectrum and by derivatization with triphenyltin chloride. Triphenyltrimethylditin was purified by crystallization, and unambiguously identified by carbon and hydrogen analysis, IR and NMR spectra. Method B also yielded a small amount of tetramethyltin as byproduct, but in no instance was any hexamethylditin observed. This finding conflicts with the earlier report, and casts some doubt on the mechanism proposed for formation of (I).

Method C involves the reaction of hexamethylditin with lithium metal[14]. A trace of tetramethyltin is noted in the resulting solution. The proton NMR spectra of trimethyltin lithium produced in all three methods are essentially identical, a single proton line absorption at $\tau = 10.4$, with tin–proton coupling constant of 5.2 cps in the case of method C, 7.5 cps in methods A and B. The difference in coupling constant is doubtless associated with the presence of lithium chloride in the solution in methods A and B.

Formation of $[(CH_3)_3Sn]_3SnLi(OC_4H_8)_3$ *(II)*

A THF solution of (I) is pumped on through a trap at dry ice-acetone bath temperature until most of the solvent has been removed. Depending on the temperature of the solution flask, this process might take several days. When the brownish black residue just begins to turn white, pumping should be stopped: solvent removal beyond this point leads to intractable solid residues along with tetramethyltin and other organotin compounds. At the point when pumping is stopped the cold trap contains solvent and tetramethyltin. Although there is always a trace of tetramethyltin in the original reaction mixture, the quantity present in the trap far exceeds that originally present.

The flask containing the solid residue is taken into an inert atmosphere box with an argon atmosphere. Benzene is added and the mixture thoroughly stirred. Filtration through several sintered glass filters yields a brownish solution and a pasty brown residue. The brown residue was not characterized in detail. When dry it is pyrophoric in air, and contains both lithium and tin. An infrared spectrum of a Nujol mull exhibited a broad peak centered at 500 cm^{-1} indicative of tin-methyl stretching modes. The solid is insoluble in THF, ether, benzene, and pentane. Removal of benzene from the filtrate solution by pumping at room temperature and below yields a yellowish-brown solid. Most of this solid is soluble in THF or benzene, but in solvent removal there is always some loss of material through decomposition. Attempts to sublime the solid recovered from benzene resulted in decomposition at about 60°, yielding mostly hexamethylditin.

If benzene removal is stopped short of completion and pentane added in large quantity, with vigorous stirring, a two-layer system is obtained. The upper layer is decanted off, and the extraction process repeated with more pentane. The combined extracts are filtered and solvent removed by pumping. On cooling down as the pumping proceeds, straw-colored needlelike crystals are formed. These are filtered and immediately transferred to a closed, dark brown bottle. The crystals which are stored thus under an argon atmosphere are stable for a period of weeks. They can be easily recrystallized from pentane if subsequent repurification should be necessary. Crystals exposed to the light, even though under an argon atmosphere, decomposed within a few hours. The crystals decompose in air.

A benzene solution of the purified material gives the proton NMR spectrum shown in Fig. 1a. This spectrum, reproduced in every detail in other preparations, is similar to the spectra of the original benzene extracts. The absorption areas due to THF are greater relative to the methyltin absorptions in the crude extract as compared with the purified samples, indicating the presence of excess THF. The centers of the THF multiplets in benzene solution of recrystallized material occur at $\tau = 6.42$ and 8.40, essentially the same values as observed for free THF in benzene.

The chemical shift values for the THF molecules in the benzene solution of the crude extract are $\tau = 6.45$ and 8.48. Since the THF absorption lines have nearly the same τ values in all three solutions, it is not feasible to determine whether exchange between free and complexed THF is occurring.

The crude extracts differ also from the solution of recrystallized material in exhibiting the small coupling constant of 2.3 cps more clearly. This coupling constant seems to vary with solvent medium; presence of slight excess THF in the benzene solutions appears to either increase the coupling constant slightly or sharpen the central line, so that the coupling is more evident. An example of the proton spectrum surrounding the central absorption in a crude benzene extract is shown in Fig. 1b.

Analysis for tin and lithium yielded the following results: Sn, 56.2, 52.7, 51.1%; Li, 0.799, 0.844, 0.847%. The tin analysis was particularly difficult because of the reactive character of the solid*. A procedure was devised for weighing the sample in cellulose capsules, then transferring to tubes, sealing off, and dissolving in fuming nitric acid. The initial reaction of the sample with the acid is violent, and difficulties were experienced in collecting all of the SnO_2 for weighing at the termination of the digestion period. It is therefore to be expected that the tin analyses will be low. The lithium analyses, on the other hand, based on flame photometric analysis of the water-soluble fraction by a standard addition technique are expected to be quite accurate. On the basis of all the data available, the compound is adjudged to have the composition $C_{21}H_{51}Sn_4O_3Li$, which leads to Sn calcd. 57.0%, Li calcd. 0.833%, in quite good agreement with the experimental results.

The IR spectrum of a nujol mull of (II) reveals the presence of characteristic methyl–tin stretching bands at 485 and 497 cm^{-1}. These are rather lower frequencies than are ordinarily observed, but are consistent with the low values observed for the

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* We are indebted to Mr. J. Nemeth for performing the analyses.

proton–tin coupling constants. It has been observed[7] that there is a rough correlation between the methyl–tin stretching frequencies and the proton–tin coupling constants. The present data follow that correlation quite well.

The proton and lithium NMR spectra of (II) are slightly different in THF than in benzene (Table 1). An aromatic solvent effect on the chemical shifts is not unexpected. The only difference other than chemical shift in the two sets of spectra is the absence of the small coupling constant about the central proton peak in the THF solutions. On the basis of a number of spectra of recrystallized material, it is quite certain that the number of THF molecules in the complex in benzene solution is three, as discussed above.

The new substance is not volatile; attempts at sublimation were not successful. Attempts to obtain a mass spectrum by warming a sample in the direct inlet system of an Atlas CH-4 yielded a series of mass peaks which could be identified with tin-containing ions. The highest mass of these occurred at 461, corresponding to $(CH_3)_7Sn_3^+$. The distribution of adjacent mass peaks was consistent with the presence of three tin atoms in the ion. The occurrence of this ion is indirect evidence for the proposed structure for (II), since it is a species one would expect on the basis of that structure.

Attempts were made to obtain identifiable products from reaction of (II) with trimethylchlorosilane in benzene and in THF. Although reaction occurred in both solvents, the proton NMR spectra of the reaction mixture revealed a complex assortment of products, none of which could be positively identified.

Reaction of (II) with triphenyltin chloride in THF at 0° led mainly to hexaphenylditin as solid product.

Reaction of (II) with methyl bromide in THF at 0° led to a complex mixture, as evidenced by the proton NMR spectrum. The presence of $[(CH_3)_3Sn]_3SnCH_3$, however, was strongly indicated by the NMR spectrum. A line at $\tau = 9.75$ has associated with its tin–proton coupling constants of 14.6, 47.0 and 48.8 cps. These are the expected chemical shift and coupling constants for the trimethyltin group protons. A line at $\tau = 9.58$, is assigned to the other methyl group protons. Its intensity is $\frac{1}{9}$ that of the line at $\tau = 9.75$. It was not possible to identify the tin–proton couplings for these protons.

Reaction of (II) with bromine in THF at −78° led to formation of trimethyltin bromide, as evidenced by the proton NMR spectrum of the reaction mixture ($\tau = 9.25$, tin–proton coupling constants of 66.4 and 63.6 cps).

Reaction with $Mn(CO)_5Br$ yielded $Mn(CO)_5Sn(CH_3)_3$ as the only metal carbonyl-containing reaction product.

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SUMMARY

Trimethylstannyllithium (I) has been prepared in THF. In the absence of lithium halide the proton resonance occurs at $\tau = 10.4$, with a tin–proton coupling

constant of 5.2 cps.

Removal of solvent THF leads to a decomposition producing tetramethyltin, an insoluble methyltin–lithium solid, and the benzene-soluble complex, tris(trimethylstannyl)stannyllithium tris(tetrahydrofuran), (II). This compound has been characterized by analysis, proton and lithium-7 NMR spectra, and chemical properties.

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