Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

HALOMETHYL–METAL COMPOUNDS

LVI*. TRIMETHYLTINDIHALOMETHYLLITHIUM REAGENTS

DIETMAR SEYFERTH, FRANK M. ARMBRECHT, JR.**, ROBERT L. LAMBERT, JR.*** and WOLFGANG TRONICH****
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (*U.S.A.*)
(Received May 5th, 1972)

SUMMARY

The preparation of trimethyltindichloromethyllithium by reaction of bis(trimethyltin)dichloromethane with n-butyllithium, of trimethyltinbromochloromethyllithium by reaction of bis(trimethyltin)bromochloromethane with n-butyllithium and of trimethyltindibromomethyllithium by reaction of trimethyl(tribromomethyl)tin or bis(trimethyltin)dibromomethane with n-butyllithium is described. All of these new lithium reagents are stable in THF-rich media only at low temperatures (−95° or below). Their reactions with trimethylchlorosilane are complicated by the fact that at such low temperatures the product, trimethylsilyl(trimethyltin)dihalomethane, is comparable in reactivity toward the lithium reagent with trimethylchlorosilane. Similar complications occur with other quenching agents such as methyl iodide.

INTRODUCTION

In recent papers of this series[3,4] we have described the preparation and utilization in synthesis of the trimethylsilyldihalomethyllithium reagents Me_3SiCCl_2Li and Me_3SiCBr_2Li (eqns. 1 and 2), as well as of the Grignard reagents Me_3SiCBr_2MgCl and Me_3SnCBr_2MgCl (eqn. 3). The action of n-butyllithium on $(Me_3Si)_2CBr_2$ at −105° gave $(Me_3Si)_2CBrLi$ in good yield. In view of this well-developed

$$Me_3SiCCl_2H + BuLi \xrightarrow{-100°} Me_3SiCCl_2Li + n\text{-}C_4H_{10} \quad (1)$$

$$Me_3SiCBr_3 + BuLi \xrightarrow{-105°} Me_3SiCBr_2Li + BuBr \quad (2)$$

$$Me_3MCBr_3 + i\text{-}PrMgCl \xrightarrow{THF,\,-85°} Me_3MCBr_2MgCl + i\text{-}PrBr \quad (3)$$

$$(M = Si,\ Sn)$$

---

[*] For Part LV see ref. 1. This paper also is Part X of the series, "The Preparation of Organolithium Reagents by the Transmetalation Reaction"; for Part IX see ref. 2.
[**] National Institutes of Health Predoctoral Fellow, 1964–1968.
[***] Air Pollution Special Fellow, 1969–1972.
[****] Postdoctoral Research Associate, 1968–1969

chemistry of trimethylsilyl-substituted halomethyllithium reagents, it seemed desirable to examine the possibility of preparing analogous trimethyltin-substituted lithium compounds. In this paper we report the successful preparation of $\mathrm{Me_3SnCCl_2Li}$, $\mathrm{Me_3SnCBr_2Li}$ and $\mathrm{Me_3SnCClBrLi}$.

At the outset, we note that polyhalomethyllithium reagents are not stable at room temperature, and this was found to be true for the trimethylsilyldihalomethyllithiums. Experience by the workers in this field[5] has shown that low reaction temperatures and THF-rich solvent systems are required in order to optimize the preparation and subsequent nucleophilic reaction chemistry of polyhalomethyllithium reagents. This also was found to be the case for the new organotin-substituted polyhalomethyllithiums which we describe here, temperatures of −95° to −120° being used in their preparation and their subsequent utilization.

RESULTS AND DISCUSSION

One could, in principle, write equations analogous to eqns. (1) and (2) for the trimethyltin case. However, nucleophilic substitution at tin is a very facile process and, indeed, the preparation of organolithium reagents by transmetalation reactions between organotin compounds and organolithiums finds useful application in some cases (eqn. 4)[6]. Such reactions proceed particularly well when R, the group displaced

$$\mathrm{Me_3SnR + R'Li \rightleftarrows RLi + Me_3SnR'} \qquad (4)$$

from tin, is an electronegative substituent (vinyl, allyl, trifluorovinyl, etc.) Thus it was no surprise to find that n-butyllithium reacted with trimethyl(dichloromethyl)tin[7] at −100° in the sense of eqn. (4) (not eqn. 1), giving n-butyltrimethyltin and dichloromethyllithium (eqn. 5). The more bulky tert-butyllithium reacted in similar

$$\begin{array}{l}\mathrm{Me_3SnCCl_2H + BuLi \longrightarrow \underset{(47\%)}{BuSnMe_3} + LiCCl_2H} \qquad (5)\\ \qquad\qquad\qquad\qquad\qquad\qquad \xrightarrow{\mathrm{Me_3SiCl}} \mathrm{Me_3SiCCl_2H}\ \ (42\%)\end{array}$$

fashion. Attempted preparation of trimethyltindibromomethyllithium by the action of dichloromethyllithium on trimethyl(dibromomethyl)tin (a reaction based on prior work of Köbrich and Fischer[8]) also failed:

$$\mathrm{Me_3SnCBr_2H + LiCCl_2H} \begin{cases} \not\longrightarrow \mathrm{Me_3SnCBr_2Li + CH_2Cl_2} \\ \longrightarrow \mathrm{\underset{(76\%)}{Me_3SnCCl_2H} + LiCBr_2H \xrightarrow{Me_3SiCl} \underset{(66\%)}{Me_3SiCBr_2H}} \end{cases} \qquad (6)$$

However, trimethyl(tribromomethyl)tin, prepared either by the reaction of $\mathrm{Me_3SnNEt_2}$ with bromoform[9] or by the action of tribromomethyllithium on trimethyltin chloride, did undergo Li/Br exchange (eqn. 7). Addition of trimethylchlorosilane to the reaction mixture gave a mixture of products: the expected $\mathrm{Me_3SiCBr_2SnMe_3}$

$$\mathrm{Me_3SnCBr_3 + BuLi \xrightarrow{-100^\circ} Me_3SnCBr_2Li + BuBr} \qquad (7)$$

in 20% yield, but also $\mathrm{(Me_3Sn)_2CBr_2}$ (17%) and $\mathrm{(Me_3Si)_2CBr_2}$ (26%). In addition, n-butyl bromide (68%) and n-butyltrimethyltin (12%) were present in the mixture. The formation of such a mixture of products at the low reaction temperatures used is readily rationalized in terms of the known[10] relatively poor reactivity of trimethylchlorosilane toward organolithium reagents, especially at low temperature[11], and the high reactivity of polyhalomethyl–tin compounds toward organolithium reagents. The process shown in eqns. (8)–(11) ($X=Br$) serves nicely to explain the products. In addition, the process most likely leading to the observed n-butyltrimethyltin

$$Me_3SnCX_2Br+BuLi \rightarrow Me_3SnCX_2Li+BuBr \tag{8}$$

$$Me_3SnCX_2Li+Me_3SiCl \rightarrow Me_3SiCX_2SnMe_3+LiCl \tag{9}$$

$$Me_3SnCX_2Li+Me_3SiCX_2SnMe_3 \rightarrow Me_3SnCX_2SnMe_3+Me_3SiCX_2Li \tag{10}$$

$$Me_3SiCX_2Li+Me_3SiCl \rightarrow Me_3SiCX_2SiMe_3+LiCl \tag{11}$$

also could contribute to the $(Me_3Si)_2CBr_2$ yield [eqns. (12)–(14), followed by eqn. (11)].

$$Me_3SnCBr_3+BuLi \rightarrow BuSnMe_3+CBr_3Li \tag{12}$$

$$CBr_3Li+Me_3SiCl \rightarrow Me_3SiCBr_3+LiCl \tag{13}$$

$$Me_3SiCBr_3+RLi \rightarrow Me_3SiCBr_2Li+RBr \tag{14}$$

In contrast to these results, the preparation of $Me_3SiCBr_2SnMe_3$ by reaction of Me_3SiCBr_2Li with trimethyltin chloride gives at most only minor amounts of $Me_3SnCBr_2SnMe_3$[4]. In this case we are dealing with a much more reactive substrate, trimethyltin chloride, and secondly, the action of Me_3SiCBr_2Li on $Me_3SiCBr_2SnMe_3$ would produce no net change, if one makes the reasonable assumption that the lithium reagent will attack selectively at tin.

The propensity of alkyllithiums to attack at tin provided the basis for another synthesis of Me_3SnCX_2Li reagents in which the bis(trimethyltin)dihalomethanes served as starting materials. Initially, these compounds were available via reaction of the respective $PhHgCCl_nBr_{3-n}$ ($n=0$–2) compound with hexamethylditin (eqn. 15)[12], but at later stages of this project, the compound $(Me_3Sn)_2CBr_2$ was prepared

$$Me_3Sn{-}SnMe_3+PhHgCl_nBr_{3-n} \rightarrow (Me_3Sn)_2CCl_nBr_{2-n}+PhHgBr \quad (n=0\text{–}2) \tag{15}$$

by reaction of Me_3SnCBr_2MgCl with trimethyltin chloride. The attack of n-butyllithium on $(Me_3Sn)_2CCl_2$, $(Me_3Sn)_2CClBr$ and $(Me_3Sn)_2CBr_2$ occurred for the most part at tin, resulting in transmetalation to produce Me_3SnCCl_2Li, $Me_3SnCClBrLi$ and Me_3SnCBr_2Li, respectively (eqn. 16).

$$Me_3SnCX_2SnMe_3+BuLi \xrightarrow{\text{low temp.}} Me_3SnCX_2Li+BuSnMe_3 \tag{16}$$

However, neither the formation of these reagents at these low temperatures, nor their subsequent reactions were straightforward and without complications, and the yields of the desired coupling products were moderate at best.

The synthesis of trimethyltindichloromethyllithium from bis(trimethyltin)dichloromethane and the reactions of this lithium reagent were studied in some detail. When the reagent obtained by reaction of $(Me_3Sn)_2CCl_2$ with a slight excess of n-butyllithium at −130° in the appropriate solvent mixture was quenched with trimethylchlorosilane, the volatile components present after work-up were found to be n-butyltrimethyltin (91%), the expected $Me_3SiCCl_2SnMe_3$ (36%), $(Me_3Si)_2CCl_2$ (19%) and $(Me_3Sn)_2CCl_2$ (35%). The high n-butyltrimethyltin yield indicated a high conversion in the transmetalation step, yet about one-third of the starting material was recovered. Here again, subsequent reaction of the initial coupling product with as yet unreacted Me_3SnCCl_2Li serves to explain both the recovery of $(Me_3Sn)_2CCl_2$ and the formation of $(Me_3Si)_2CCl_2$: eqns. (10) and (11), with X = Cl. Similar complications were encountered when the reaction mixture containing Me_3SnCCl_2Li was quenched with methyl iodide. A 78% yield of n-butyltrimethyltin was obtained, yet $Me_3SnCCl_2SnMe_3$ was recovered in 37% yield. The methylated product, $Me_3SnCCl_2CH_3$, was obtained in 26% yield. Inverse addition of the lithium reagent solution to methyl iodide was technically difficult and gave even lower yields (17–19%) of $Me_3SnCCl_2CH_3$. Hydrolysis of such a Me_3SnCCl_2Li-containing solution produced trimethyl(dichloromethyl)tin in 54% yield.

When bis(trimethyltin)dibromomethane was treated with one molar equivalent of n-butyllithium at low temperature, even more complications were encountered. In contrast to the $Me_3SnCCl_2SnMe_3$/BuLi reactions, here the n-butyltrimethyltin yields were low, and furthermore were dependent upon transmetalation reaction time. Short (15–30 min) reaction times gave the highest n-butyltrimethyltin yields (up to 57%), while long (9–12 h) reaction times resulted in quite low (5–12%) yields of this compound. Yet long reaction times appeared to give the highest yields of Me_3SnCBr_2Li as measured by the yields (up to 50%) of $Me_3SiCBr_2SnMe_3$ obtained on quenching with trimethylchlorosilane. Although the recovered $(Me_3Sn)_2CBr_2$ yields were substantial (50–15%, depending on the length of the reaction time), the $(Me_3Si)_2CBr_2$ yields were quite low (< 10%), which suggests that the major part of recovered $(Me_3Sn)_2CBr_2$ is unconsumed, not regenerated, material. Also, another product, di-n-butyldimethyltin, was found to be present in the reaction mixture. These findings are best accommodated by the following picture. The transmetalation reaction [eqn. (16), X = Br] either proceeds substantially to completion but only at a very slow rate, or the equilibrium is unfavorable. Whichever possibility is correct (we favor the former), this allows another transmetalation involving already formed n-butyltrimethyltin to take place (eqn. 17). As the reaction time is extended, more and

$$BuSnMe_3 + BuLi \rightarrow MeLi + Bu_2SnMe_2 \qquad (17)$$

more n-butyltrimethyltin is consumed in this way, but the methyllithium formed can (as a separate experiment showed) also attack $(Me_3Sn)_2CBr_2$ to generate Me_3SnCBr_2Li. Such a decreased reactivity of $(Me_3Sn)_2CBr_2$ might have been expected in view of the observation made with trimethyl(tribromomethyl)tin that more n-butyllithium attack occurs at bromine than at tin. Hydrolysis of Me_3SnCBr_2Li-containing solutions gave the expected Me_3SnCBr_2H.

Essentially the same observations were made with $Me_3SnCClBrSnMe_3$, whose reaction with n-butyllithium at low temperature gave trimethyltinchlorobromomethyllithium. Addition of trimethylchlorosilane to such a reagent solution gave $Me_3SiCClBrSnMe_3$ in 49% yield, while hydrolysis produced $Me_3SnCClBrH$. Again, di-n-butyldimethyltin was present, and the amount of $(Me_3Si)_2CClBr$ formed during the reaction with trimethylchlorosilane was small.

In conclusion, this investigation has shown that the trimethyltindihalomethyllithium reagents can be made either by the lithium/bromine exchange reaction or by the transmetalation reaction and that they are stable in THF-rich medium at low temperatures. Their reactions with substrates such as trimethylchlorosilane and methyl iodide are complicated by competing attack of the Me_3SnCX_2Li reagent at the tin atom in the coupling product. Nevertheless, these new reagents may allow the preparation of organotin compounds whose synthesis by other routes might be difficult or impossible to realize.

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of dry nitrogen or argon in flame-dried glassware. The preparation of lithium reagents at low temperature was carried out in a three-necked Morton (creased) flask of suitable volume equipped with a high-speed stirrer ("Stir-O-Vac", Labline catalog no. 1280), a pentane thermometer and an addition funnel with pressure-equalizing side-arm topped with a gas inlet tube (henceforth "standard apparatus"). All solvents were dried prior to use, THF, pentane and diethyl ether by distillation from lithium aluminum hydride. Dimethyl ether, a gas, was dried by passing it through a drying tower containing activated alumina (Woelm neutral), anhydrous calcium sulfate and P_4O_{10}.

n-Butyllithium was purchased in hexane solution from the Foote Mineral Co. or from Alfa Inorganics. Trimethylchlorosilane was obtained from Union Carbide Corp., trimethyltin chloride from M & T Chemicals, Inc.

Infrared spectra were recorded using a Perkin Elmer Model 337 or 237B grating infrared spectrophotometer, NMR spectra using either a Varian Associates A60 or T60 NMR spectrometer. Unless otherwise stated, chloroform was used as an internal standard and related to an external chloroform/TMS sample. Chemical shifts are expressed in δ units, ppm downfield from TMS. Gas chromatography (GLC) was used extensively for separation and purification of products and for yield determinations. The instruments used included the MIT isothermal unit and F & M Model 700, 720 and 5754 gas chromatographs. The internal standard method was used in yield determinations.

Reaction of trimethyl(dichloromethyl)tin with n-butyllithium

The standard apparatus was charged with 6.3 ml (10.3 mmol) of 1.63 *N* BuLi and 35 ml of 3/1/1/1 THF/diethyl ether/methylal*/pentane solvent mixture. Another 25 ml of solvent mixture containing 2.46 g (10.0 mmol) of Me_3SnCCl_2H[7] was added over 40 min. to the stirred BuLi solution at −110° to −130°C. The mixture was stirred for 95 min, and then 1.15 g (10.6 mmol) of trimethylchlorosilane was added rapidly. After 30 min, the reaction mixture was allowed to warm to room temperature. Addition of 10 ml of dry dioxane precipitated the lithium chloride from the solution. Filtration was followed by concentration of the filtrate at reduced pressure. The remaining solution was trap-to-trap distilled at 0.6 mmHg (room temperature) to give 8.64 g of clear liquid, whose GLC analysis (20% SE-30 at 80–110°) indicated

---

* Methylal = dimethoxymethane.

the presence of Me_3SiCCl_2H[3] (42%), $BuSnMe_3$ (47%) and Me_3SnCCl_2H (34%). All products were identified by comparison of their GLC retention times and IR spectra with those of authentic samples.

A similar reaction of Me_3SnCCl_2H with tert-butyllithium (Lithium Corp. of America) followed by treatment of the reagent present with trimethylchlorosilane gave Me_3SiCCl_2H (46%), Me_3SnCMe_3 (50%: identified by comparison with an authentic sample supplied by Dr. G. Reifenberg of M & T Chemicals, Inc.) and Me_3SnCCl_2H (38%).

Reaction of trimethyl(dibromomethyl)tin with dichloromethyllithium

The standard apparatus was charged with 8.5 g (0.1 mol) of dichloromethane and 70 ml of dry THF and cooled to −95°. n-Butyllithium (28.8 mmol) in hexane was added during 5 min. After the mixture had been stirred for 15 min, 8.43 g (25.0 mmol) of trimethyl(dibromomethyl)tin[4] was added and the resulting mixture was stirred at −95° for 30 min, and subsequently was treated with 31 mmol of trimethylchlorosilane. After it had been stirred at −95° for 80 min, the reaction mixture was allowed to warm to room temperature. Trap-to-trap distillation at 0.05 mmHg and room temperature was followed by extraction of the residue with 15 ml of hexane and 40 ml of water. The combined distillate and hexane layer were analyzed by GLC (20% SE-30). Trimethyl(dichloromethyl)tin (76%) and trimethyl(dibromomethyl)silane[4] (66%) were present. These compounds were identified on the basis of their GLC retention times and IR spectra.

Reaction of trimethyl(tribromomethyl)tin with n-butyllithium

The standard reaction apparatus was charged with 33.0 g (0.10 mol) of carbon tetrabromide and 200 ml of dry THF and cooled to −95°. A solution of n-butyllitium (104 mmol) in hexane was added slowly while the temperature was lowered to about −103°. After the mixture had been stirred for 15 min, trimethyltin chloride, 20.0 g (0.10 mol) in 50 ml of THF was added. The reaction mixture was stirred at −103° for 2½ h, warmed to room temperature and transferred under nitrogen to a distilling flask. Trap-to-trap distillation to remove volatiles followed. The residue was dissolved in 200 ml of hot hexane and crystallized at −10°. The supernatant solution was decanted and the solid remaining (24.0 g, 57%) was dissolved in 100 ml of dry THF. An NMR spectrum of an aliquot of this solution showed only a single Me_3Sn resonance at 0.52 ppm.

This solution of Me_3SnCBr_3 was charged into the standard apparatus, together with 50 ml of THF and 50 ml of diethyl ether. Cooling to −105° was followed by addition of 64 mmol of n-butyllithium in hexane. The reagent mixture was stirred at −105° for 20 min and then treated with 0.30 mol of trimethylchlorosilane. After it had been stirred for 2½ h, the mixture was allowed to warm to room temperature and trap-to-trap distilled at 0.01 mmHg (pot temperature to 70°). Analysis of the distillate by GLC (10% Union Carbide UC-W98, 90–180°) showed the presence of 44.1 mmol of n-butyl bromide (77%, based on Me_3SnCBr_3), 13.5 mmol of n-butyltrimethyltin (24%, based on Me_3SnCBr_3), 8.3 mmol of $(Me_3Si)_2CBr_2$[4], 17.6 mmol of $Me_3SiCBr_2SnMe_3$[4] (31%, based on Me_3SnCBr_3) and 10.4 mmol of $(Me_3Sn)_2CBr_2$[12] (36%, based on Me_3SnCBr_3). This represents an accounting of 91% of charged Me_3Sn groups and 90% of charged n-butyl groups. The products were identified on the basis of their

GLC retention times and IR spectra. Authentic samples were available for comparison.

In another similar reaction, the trimethyl(tribromomethyl)tin used was prepared by the method of Davies and Mitchell[9]. Very similar results were obtained.

Reaction of bis(trimethyltin)dichloromethane with n-butyllithium

The standard apparatus was charged with 4.22 g (10.2 mmol) of the tin compound and 60 ml of 3/1/1/1 THF/Et_2O/methylal/pentane. This mixture was cooled to −130° and 11.9 mmol of n-butyllithium in hexane was added. No color change was observed. The reagent mixture was stirred at −133° to −116° for 3½ h, and then 18.0 mmol of trimethylchlorosilane was added. After 30 min the reaction mixture was allowed to warm to room temperature and 10 ml of dry dioxane was added. Filtration and concentration of the filtrate at reduced pressure gave a residue which was trap-to-trap distilled at 0.03 mmHg (pot temperature to 80°). GLC analysis of the distillate (20% SE-30, 108°) showed the following to be present: n-butyltrimethyltin (91%), $(Me_3Si)_2CCl_2$[3] (1.93 mmol, 19%, based on CCl_2 groups), $Me_3SiCCl_2SnMe_3$[3] (3.71 mmol, 36% based on CCl_2 groups) and $(Me_3Sn)_2CCl_2$ (3.54 mmol, 35%). Product identification was made by means of GLC retention times and IR spectra; authentic samples were available.

A similar reaction in which the transmetalation time was only 90 min gave n-butyltrimethyltin (58%), $(Me_3Si)_2CCl_2$ (8%), $Me_3SiCCl_2SnMe_3$ (21%) and $(Me_3Sn)_2CCl_2$ (34%).

Another reaction mixture containing Me_3SnCCl_2Li (from 5.05 mmol each of $(Me_3Sn)_2CCl_2$ and n-butyllithium at −120° for 5½ h) was treated with 3.54 g (24.9 mmol) of methyl iodide for 1 h. The usual work-up gave a trap-to-trap distillate which contained (by GLC) n-butyltrimethyltin (78%), $Me_3SnCCl_2CH_3$[7] (26%) and $(Me_3Sn)_2CCl_2$ (37%). Addition of 5.4 ml of 1.0 *N* HCl to another solution of Me_3SnCCl_2Li [from 4.98 mmol of $(Me_3Sn)_2CCl_2$ and 5.7 mmol of n-butyllithium at −125° for 4½ h] gave an organic layer which was dried and analyzed by GLC. The following were present: n-butyltrimethyltin (89%), Me_3SnCCl_2H (54%) and starting tin compound in small amount.

Reaction of bis(trimethyltin)bromochloromethane with n-butyllithium

The standard apparatus was charged with 2.38 g (5.23 mmol) of $(Me_3Sn)_2CClBr$[12] and 50 ml of the usual 3/1/1/1 solvent mixture. The solution was cooled to −97° and 5.0 mmol of n-butyllithium in hexane was added over 8 min to give a bright yellow solution. The reagent mixture was stirred for 5 h at −97° and then 19.9 mmol of trimethylchlorosilane was added. The yellow color was discharged. Dioxane (5 ml) was added and the mixture was allowed to warm to room temperature. Filtration was followed by GLC analysis of the filtrate (20% SE-30, 80–210°). The following were present: n-butyltrimethyltin (56%), $(Me_3Sn)_2CClBr$ (17%), a minor amount of what probably was $(Me_3Si)_2CClBr$ (not identified) and the expected product. $Me_3SiCClBrSnMe_3$ (49%). An analytical sample of the latter was obtained by concentrating the filtrate at reduced pressure and trap-to-trap distilling (0.03 mmHg, to 80°) the residue and preparative GLC of the latter. The pure product had n_D^{25} 1.5183. (Found: C, 23.04; H, 4.95; 7.26 mg AgX from a 7.985 mg sample. $C_7H_{18}BrClSiSn$ calcd.: C, 23.07; H, 5.30%; 7.30 mg AgX from the sample taken.) IR (CS_2, cm^{-1}): 2980 (sh), 2960 m, 2900 m, 1400 m, 1267 m, 1250 s, 1188 w, 865 s, 840 s, 770 s, 740 (sh), 701 w, 690 w, 668 w, 664 w, 616 w, 598 m, 526 m. NMR ($CHCl_3$): δ 0.22 (s, 9 H, Me_3Si), 0.35 ppm [s, 9 H, Me_3Sn, $J(^{117}Sn-^1H)$ 52 Hz, $J(^{119}Sn-^1H)$ 54.5 Hz].

A solution of $Me_3SnCClBrLi$ prepared in this manner from 5.04 mmol of $(Me_3Sn)_2CClBr$ and 4.8 mmol of n-butyllithium at −97° was hydrolyzed with 5 ml of 0.997 *N* HCl in 4 ml of THF. The dried organic layer was concentrated and trap-to-trap distilled at 0.04 mmHg (pot temperature to 110°). GLC analysis of the distillate showed the presence of n-butyltrimethyltin (48 %), $(Me_3Sn)_2CClBr$ (18 %) and $Me_3SnCClBrH$ (28 %). Among several minor products which were identified were di-n-butyldimethyltin and $(Me_3Sn)_2CHCl$.

$Me_3SnCClBrH$. (Found: C, 16.12; H, 3.33. Calcd. for $C_4H_{10}BrClSn$: C, 16.44; H, 3.45 %.) IR (CS_2, cm^{-1}): 2980 w, 2910 w, 2460–2420 w, 1390 w, 1193 m, 1174 s, 1058 m, 780 vs, 711 vs, 619 vs, 534 vs. NMR($CHCl_3$): δ 0.34 [s, 9 H, Me_3Sn, $J(^{117}Sn-^1H)$ 54.5 Hz, $J(^{119}Sn-^1H)$ 57 Hz], 5.43 ppm [s, 1 H, J(Sn–H) 12 Hz].

An authentic sample of $Me_3SnCClBrH$ was prepared in 33 % yield by the reaction of $CHClBrMgCl$[4] (from 0.20 mol each of i-PrMgCl and $HCClBr_2$ in THF at −90°) with trimethyltin chloride (0.17 mol). The usual hydrolytic work-up procedure[4] gave the desired product, b.p. 75–77°/10 mmHg. A final GLC purification yielded material whose IR spectrum was identical to that tabulated above, n_D^{25} 1.5279.

Preparation of bis(trimethyltin)dibromomethane by the Grignard procedure

The standard apparatus was charged with 46.5 g (0.112 mol) of Me_3SnCBr_3[9] (transferred under nitrogen) and 200 ml of dry THF. The resulting suspension was cooled to −95° and a solution of isopropylmagnesium chloride (from 0.123 g atom of Mg in 60 ml of THF) was added over a 10 min period. The mixture was stirred for 15 min and then 21.0 g (0.1 mol) of trimethyltin chloride in 30 ml of THF was added slowly; the green-yellow color of the reagent solution was discharged. The reaction mixture was stirred at −95° for 90 min, allowed to warm slowly to room temperature and hydrolyzed to the lump point with saturated ammonium chloride solution. The organic layer was evaporated under reduced pressure and the residue was trap-to-trap distilled at 0.05 mmHg (pot temperature to 90°). Short-path distillation of the distillate gave 34.04 g (61%) of $(Me_3Sn)_2CBr_2$, b.p. 67–70°/0.03 mmHg, whose IR spectrum was identical to that of material prepared by the $PhHgCBr_3/Me_6Sn_2$ reaction[12].

Reaction of bis(trimethyltin)dibromomethane with n-butyllithium

The standard apparatus was charged with 2.26 g (4.6 mmol) of $(Me_3Sn)_2CBr_2$, 75 ml of dry THF and 25 ml of dry dimethyl ether* at −110° and 5.4 mmol of n-butyllithium in hexane was added. The resulting yellow solution was stirred at −110° for 12 h and then treated with 5.3 g (47 mmol) of trimethylchlorosilane. The reaction mixture was stirred at −110° for 90 min. Dioxane (5 ml) was added and after the mixture had stood overnight it was filtered to remove the LiCl–dioxane complex. The filtrate was concentrated at reduced pressure to remove solvent and then was trap-to-trap distilled at 0.01 mmHg (pot temperature to 110°). GLC analysis (20% DC-

---

* The preferred solvent system for low temperature lithium chemistry; *cf.* ref. 13.

200, 180°) showed the presence of n-butyltrimethyltin (5%), $Me_3SiCBr_2SnMe_3$[4] (51%) and $(Me_3Sn)_2CBr_2$ (30%).

In another similar reaction in which the transmetalation reaction time was 9 h, the product yields were: n-butyltrimethyltin, 12%, $Me_3SiCBr_2SnMe_3$, 49%, $(Me_3Sn)_2CBr_2$, 17%. A 2½ h transmetalation time (same procedure) gave these products in yields of 39%, 36% and 27%, respectively. A 5½ h reaction time gave them in yields of 35%, 44% and 12%, respectively. Minor amounts of di-n-butyldimethyltin and $(Me_3Si)_2CBr_2$ were present in these reaction mixtures.

A solution of Me_3SnCBr_2Li [from 10.4 mmol of $(Me_3Sn)_2CBr_2$ and 10.5 mmol of n-butyllithium in 85 ml of THF and 25 ml of dimethyl ether at −120° for 5 h] was treated with aqueous THF. The deep yellow color was discharged and the reaction mixture was dried over $MgSO_4$. GLC analysis (20% SE-30, 90–197°) showed the presence of n-butyltrimethyltin (47%), trimethyl(dibromomethyl)tin[4] (27%), $(Me_3Sn)_2CBr_2$ (10%) and minor amounts of di-n-butyldimethyltin and $(Me_3Sn)_2CHBr$. (Found: C, 20.50; H, 4.77. $C_7H_{19}BrSn_2$ calcd.: C, 19.99; H, 4.55%). The IR spectrum of the latter showed (CS_2, cm^{-1}): 2980 s, 2910 s, 2355 w, 1715 w, 1695 w, 1390 m, 1195 (sh), 1187 s, 1078 m, 942 s, 878 w, 770 vs, 710 vs, 622 vs. The NMR spectrum of the known[4] Me_3SnCBr_2H was recorded (in $CHCl_3$): δ 0.46 [s, 9 H, $J(^{117}Sn-^{1}H)$ 54 Hz, $J(^{119}Sn-^{1}H)$ 56.5 Hz] and 5.40 ppm [s, 1 H, $J(Sn-H)$ 12 Hz]. The NMR spectrum of $(Me_3Sn)_2CHBr$ showed (in CS_2): δ 0.20 [s, 18 H, $J(^{117}Sn-^{1}H)$ 51.5 Hz, $J(^{119}Sn-^{1}H)$ 53.5 Hz] and 2.60 ppm [s, 1 H, $J(Sn-H)$ 35 Hz].

Thermal decomposition of the trimethyltindihalomethyllithium reagents

A flame-dried Pyrex test tube under an atmosphere of dry nitrogen was charged with ca. 0.7 mmol of the respective bis(trimethyltin)dihalomethane, 3 ml of dry THF and 1 ml of dry dimethyl ether and three glass beads. The tube was capped with a no-air stopper and cooled to −123°. Ca. 0.72 mmol of n-butyllithium in hexane was added with a syringe and the reaction was allowed to proceed (with shaking) for 30 min. Then the temperature was allowed to rise very slowly. The following visual observations were made.

Me_3SnCCl_2Li. The initially pale yellow solution (at −123°) began to darken to orange at about −75° and turned black(indicating complete decomposition) between −65° and −55°.

$Me_3SnCClBrLi$. The initially pale yellow solution deepened slightly to orange at −100°, to dark orange at −90°. After standing 1 min at −80°, it became black but translucent. It was opaque at −70°.

Me_3SnCBr_2Li. The initially yellow solution darkened to orange-yellow slowly between −120° and −85° and much more rapidly at −80°. The solution was orange-brown at −75° and orange-black at −65°. It became opaque at −55°.

ACKNOWLEDGEMENTS

The authors are grateful to the U.S. Air Force Office of Scientific Research (NC)-OAR (Grant AF-AFOSR-72-2204) and to the National Science Foundation (Grant GP 31429X) for generus support of this work and to Union Carbide Corp. and M & T Chemicals, Inc. for gifts of chemicals. Fellowship support by the National Institutes of Health to F.M.A. (PHS Fellowship 5-F1-GM-23,742) and by the

Environmental Protection Agency to R.L.L. (5-F03-AP-36,021) is gratefully acknowledged.

REFERENCES

1 D. Seyferth and S. P. Hopper, *J. Organometal. Chem.*, 44 (1972) 97.
2 D. Seyferth, R. Suzuki, C. J. Murphy and C. R. Sabet, *J. Organometal. Chem.*, 2 (1964) 431.
3 D. Seyferth, E. M. Hanson and F. M. Armbrecht Jr., *J. Organometal. Chem.*, 23 (1970) 361.
4 D. Seyferth, R. L. Lambert Jr. and E. M. Hanson, *J. Organometal. Chem.*, 24 (1970) 647.
5 G. Köbrich, *Angew. Chem., Int. Ed. Eng.*, 6 (1967) 41; *Bull. Soc. Chim. Fr.*, (1969) 2712 (reviews).
6 D. Seyferth, M. A. Weiner, L. G. Vaughan, G. Raab, D. E. Welch, H. M. Cohen and D. L. Alleston, *Bull. Soc. Chim. Fr.*, (1963) 1364 (review).
7 D. Seyferth and F. M. Armbrecht Jr., *J. Organometal. Chem.*, 16 (1969) 249.
8 G. Köbrich and R. H. Fischer, *Chem. Ber.*, 101 (1968) 3208.
9 A. G. Davies and T. N. Mitchell, *J. Chem. Soc. C.* (1969) 1896.
10 A. E. Bey and D. R. Weyenberg, *J. Org. Chem.*, 31 (1966) 2036.
11 W. R. Bamford and B. C. Pant, *J. Chem. Soc. C*, (1967) 1470.
12 D. Seyferth, F. M. Armbrecht Jr. and B. Schneider, *J. Amer. Chem. Soc.*, 91 (1969) 1954.
13 D. Seyferth, D. C. Mueller and F. M. Armbrecht Jr., *Organometal. Chem. Syn.*, 1 (1970) 3.