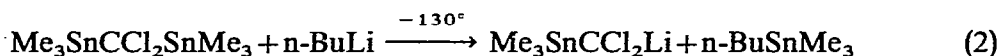


## PRELIMINARY NOTE

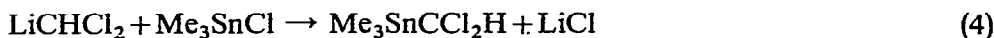
### Novel organosilicon- and organotin-substituted polychloromethylithium reagents: $(\text{CH}_3)_3\text{SiCCl}_2\text{Li}$ and $(\text{CH}_3)_3\text{SnCCl}_2\text{Li}$

Much effort has been devoted in recent years to the preparation and synthetic utilization of polyhalomethylithium reagents such as  $\text{CCl}_3\text{Li}$ <sup>1</sup>,  $\text{CHCl}_2\text{Li}$ <sup>2</sup>,  $\text{PhCCl}_2\text{Li}$ <sup>1b</sup>, etc. Our interest in polyhalomethyl derivatives of silicon and tin<sup>3-6</sup> has led us to prepare trimethylsilyldichloromethylithium and trimethyltindichloromethylithium by the procedures shown in eqns. 1 and 2. These reactions were carried out in a



standard solvent mixture of three parts THF, and one part each of diethyl ether, methylal and pentane<sup>7</sup>, and they proceeded in high yield. The reaction of trimethyl-(dichloromethyl)tin\* with *n*-butyl- or *tert*-butyllithium resulted in nucleophilic attack at tin with displacement of the dichloromethyl group, rather than in proton abstraction as in the case of trimethyl(dichloromethyl)silane\*\*. The availability of bis(trimethyltin)dichloromethane<sup>9</sup> and the ready displacement of electronegative organic substituents from tin by alkylolithiums, however, made possible the high yield synthesis of  $\text{Me}_3\text{SnCCl}_2\text{Li}$  as shown in eqn. 2.

Both of these novel organolithium reagents undergo usual RLi reactions, but in both cases interesting complications were encountered. The reaction of trimethylsilyldichloromethylithium with methyl iodide gave the expected  $\text{Me}_3\text{SiCCl}_2\text{-Me}$ , m.p. 117–119°, in 77% yield, but a by-product in 11% yield was  $\text{Me}_3\text{SiCCl}_2\text{SiMe}_3$ ,  $n_D^{25}$  1.4667. Similarly, in the reaction of  $\text{Me}_3\text{SiCCl}_2\text{Li}$  with trimethyltin chloride, which gave  $\text{Me}_3\text{SiCCl}_2\text{SnMe}_3$ , a liquid, b.p. 84°/10 mm,  $n_D^{25}$  1.4992, in 70% yield, two by-products,  $\text{Me}_3\text{SiCCl}_2\text{SiMe}_3$  (17%, based on available  $\text{Me}_3\text{Si}$  groups) and  $\text{Me}_3\text{SnCCl}_2\text{H}$  (10%), were formed. This by-product formation is explicable as shown in eqns. 3 and 4. Further support for this explanation was given by independent observation of the process indicated by eqn. 3.

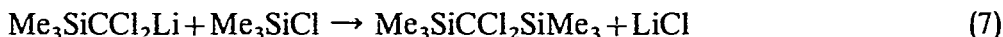
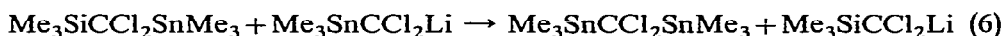
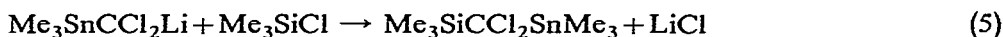


\* A liquid, b.p. 86–87°/38 mm, prepared in 66% yield by the reaction of dichloromethylithium and trimethyltin chloride. NMR: singlets at 0.3 ppm (9 H) and 5.4 ppm (1 H) downfield from TMS, with the expected side bands due to Sn–C–H spin–spin coupling.

\*\* This provides still another example of the difference in behavior between silicon and tin compounds toward organolithium reagents, i.e., attack at tin in the organotin compound and at other sites in the molecule in the corresponding silane. Note, for instance, the action of phenyllithium on the vinyltriphenyl derivatives of silicon, germanium and tin<sup>8</sup>.

The bromination of trimethylsilyldichloromethyl lithium gave only a 7% yield of trimethyl(bromodichloromethyl)silane, m.p. 152–153°, together with a 45% yield of  $\text{Me}_3\text{SiCCl}_2\text{SiMe}_3$ , when bromine was added to the lithium reagent solution at  $-125^\circ$ . However, addition of the  $\text{Me}_3\text{SiCCl}_2\text{Li}$  solution to a fivefold excess of bromine in ether resulted in the formation of  $\text{Me}_3\text{SiCCl}_2\text{Br}$  in 45% yield, and only a 5% by-product yield was noted. In this case it would seem that an added complication is that as yet unconverted  $\text{Me}_3\text{SiCCl}_2\text{Li}$  is capable of reacting with the  $\text{Me}_3\text{-SiCCl}_2\text{Br}$  produced to give  $\text{Me}_3\text{SiCCl}_2\text{SiMe}_3$  by displacement of the  $\text{CCl}_2\text{Br}$  group from silicon.

Competing reactions of the organolithium reagent with substrate and product also complicated the preparative utilization of trimethyltindichloromethyl lithium. The reaction mixture obtained by quenching the reagent prepared from 10.2 mmoles of bis(trimethyltin)dichloromethane and 11.9 mmoles of n-butyllithium with trimethylchlorosilane (12.4 mmoles) was found via GLPC to contain n-butyltrimethyltin (91%),  $\text{Me}_3\text{SiCCl}_2\text{SiMe}_3$  (19%),  $\text{Me}_3\text{SiCCl}_2\text{SnMe}_3$  (36%) and  $\text{Me}_3\text{SnCCl}_2\text{SnMe}_3$  (35%). At first sight, the nearly quantitative yield of n-butyltrimethyltin and the 35% recovery of  $\text{Me}_3\text{SnCCl}_2\text{SnMe}_3$  are in mutual contradiction. However, the reaction sequence below, which follows eqn. 2, the generation of  $\text{Me}_3\text{SnCCl}_2\text{Li}$  and n-butyltrimethyltin in 91% yield, explains the results obtained:



Thus the  $\text{Me}_3\text{SnCCl}_2\text{SnMe}_3$  recovered does not represent unconverted starting material and is instead the product of the reaction sequence (1)–(5)–(6). Similarly, quenching of the reagent from the  $\text{n-BuLi}^+\text{Me}_3\text{SnCCl}_2\text{SnMe}_3$  reaction with methyl iodide gave a mixture of n-butyltrimethyltin (78%),  $\text{Me}_3\text{SnCCl}_2\text{SnMe}_3$  (37%) and the expected product,  $\text{Me}_3\text{SnCCl}_2\text{Me}$  (26%)\*. Hydrolysis of  $\text{Me}_3\text{SnCCl}_2\text{Li}$  with 1.0 N HCl at  $-120^\circ$  resulted in formation of trimethyl(dichloromethyl)tin in 54% yield.

In spite of these complications due to the relatively easily achieved displacement of polychlorinated substituents from silicon and tin by organolithium reagents, trimethylsilyl- and trimethyltindichloromethyl lithium are useful reagents which make possible the preparation of novel chlorinated organosilicon and organotin compounds. Further work concerned with the preparative application of these reagents is in progress, and full details will be reported at a later date. Satisfactory analytical data were obtained for all the new compounds mentioned in this communication.

#### Acknowledgments

The authors are grateful to the U.S. Army Research Office (Durham) for generous support of this work and to M & T Chemicals, Inc. for gifts of chemicals.

\* An authentic sample of trimethyl(1,1-dichloroethyl)tin, m.p. 58–59°, was prepared in 47% yield by the reaction of trimethyltin chloride with  $\text{MeCCl}_2\text{Li}$  (prepared by reaction of n-butyllithium with 1,1-dichloroethane in the standard solvent mixture at  $-115^\circ$ ). NMR: singlets at 0.30 ppm [9 H;  $J(^{117}\text{Sn}-^1\text{H})$  53 cps;  $J(^{119}\text{Sn}-^1\text{H})$  55 cps] and 2.17 ppm [3 H;  $J(\text{Sn}-\text{H})$  35 cps].

This investigation was supported in part by Public Health Service Fellowships 5-F1-GM-23,742 (to F.M.A.) and 5-F1-GM-28,934 (to E.M.H.).

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Received August 24th, 1967

*J. Organometal. Chem.*, 10 (1967) P25-P27