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PRELIMINARY NOTE

Novel organosilicon- and organotin-substituted polychloromethyllithium reagents: $(CH_3)_3SiCCl_2Li$ and $(CH_3)_3SnCCl_2Li$

Much effort has been devoted in recent years to the preparation and synthetic utilization of polyhalomethyllithium reagents such as CCl_3Li[1], $CHCl_2Li$[2], $PhCCl_2Li$[1b], etc. Our interest in polyhalomethyl derivatives of silicon and tin[3-6] has led us to prepare trimethylsilyldichloromethyllithium and trimethyltindichloromethyllithium by the procedures shown in eqns. 1 and 2. These reactions were carried out in a

$$Me_3SiCCl_2H + PhLi \xrightarrow{-125^\circ} Me_3SiCCl_2Li + C_6H_6 \tag{1}$$

$$Me_3SnCCl_2SnMe_3 + n\text{-}BuLi \xrightarrow{-130^\circ} Me_3SnCCl_2Li + n\text{-}BuSnMe_3 \tag{2}$$

standard solvent mixture of three parts THF, and one part each of diethyl ether, methylal and pentane[7], 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[9] and the ready displacement of electronegative organic substituents from tin by alkyllithiums, however, made possible the high yield synthesis of Me_3SnCCl_2Li 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 trimethylsilyldichloromethyllithium with methyl iodide gave the expected Me_3SiCCl_2Me, m.p. 117–119°, in 77% yield, but a by-product in 11% yield was $Me_3SiCCl_2SiMe_3$, n_D^{25} 1.4667. Similarly, in the reaction of Me_3SiCCl_2Li with trimethyltin chloride, which gave $Me_3SiCCl_2SnMe_3$, a liquid, b.p. 84°/10 mm, n_D^{25} 1.4992, in 70% yield, two by-products, $Me_3SiCCl_2SiMe_3$ (17%, based on available Me_3Si groups) and Me_3SnCCl_2H (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.

$$Me_3SiCCl_2Li + Me_3SiCCl_2H \rightarrow Me_3SiCCl_2SiMe_3 + LiCHCl_2 \tag{3}$$

$$LiCHCl_2 + Me_3SnCl \rightarrow Me_3SnCCl_2H + LiCl \tag{4}$$

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* A liquid, b.p. 86–87°/38 mm, prepared in 66% yield by the reaction of dichloromethyllithium 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[8].

The bromination of trimethylsilyldichloromethyllithium gave only a 7% yield of trimethyl(bromodichloromethyl)silane, m.p. 152–153°, together with a 45% yield of $Me_3SiCCl_2SiMe_3$, when bromine was added to the lithium reagent solution at −125°. However, addition of the Me_3SiCCl_2Li solution to a fivefold excess of bromine in ether resulted in the formation of Me_3SiCCl_2Br 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 Me_3SiCCl_2Li is capable of reacting with the Me_3SiCCl_2Br produced to give $Me_3SiCCl_2SiMe_3$ by displacement of the CCl_2Br group from silicon.

Competing reactions of the organolithium reagent with substrate and product also complicated the preparative utilization of trimethyltindichloromethyllithium. 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%), $Me_3SiCCl_2SiMe_3$ (19%), $Me_3SiCCl_2SnMe_3$ (36%) and $Me_3SnCCl_2SnMe_3$ (35%). At first sight, the nearly quantitative yield of n-butyltrimethyltin and the 35% recovery of $Me_3SnCCl_2SnMe_3$ are in mutual contradiction. However, the reaction sequence below, which follows eqn. 2, the generation of Me_3SnCCl_2Li and n-butyltrimethyltin in 91% yield, explains the results obtained:

$$Me_3SnCCl_2Li + Me_3SiCl \rightarrow Me_3SiCCl_2SnMe_3 + LiCl \quad (5)$$

$$Me_3SiCCl_2SnMe_3 + Me_3SnCCl_2Li \rightarrow Me_3SnCCl_2SnMe_3 + Me_3SiCCl_2Li \quad (6)$$

$$Me_3SiCCl_2Li + Me_3SiCl \rightarrow Me_3SiCCl_2SiMe_3 + LiCl \quad (7)$$

Thus the $Me_3SnCCl_2SnMe_3$ 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 n-BuLi+$Me_3SnCCl_2SnMe_3$ reaction with methyl iodide gave a mixture of n-butyltrimethyltin (78%), $Me_3SnCCl_2SnMe_3$ (37%) and the expected product, Me_3SnCCl_2Me (26%)*. Hydrolysis of Me_3SnCCl_2Li with 1.0 *N* HCl at −120° 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 trimethyltindichloromethyllithium 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.

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* 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 $MeCCl_2Li$ (prepared by reaction of n-butyllithium with 1,1-dichloroethane in the standard solvent mixture at −115°). NMR: singlets at 0.30 ppm [9 H; $J(^{117}Sn-^{1}H)$ 53 cps; $J(^{119}Sn-^{1}H)$ 55 cps] and 2.17 ppm [3 H; $J(Sn-H)$ 35 cps].

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