chloride reacted with 4.3 g (0.026 mole) of hydrogen polysulfide to form bis(triphenyltin) sulfide, m.p. 144–6° (lit.[7] m.p. 145–6°). The infrared spectrum was identical with those listed in the literature[4].

Hydrogen polysulfide and diallyldi-n-butyltin

Similarly, 15.5 g (0.049 mole) of diallyldi-*n*-butyltin reacted with 9.0 g (0.055 mole) of hydrogen polysulfide. A non-distillable product was obtained $[(n\text{-}C_4H_9)_2SnS_{1.6}]_3$. (Found: C, 34.03; H, 6.07; S, 17.99; Sn, 41.32; mol. wt., 808. $C_{24}H_{54}Sn_3S_{4.8}$ calcd.: C, 33.80; H, 6.33; S, 17.96; Sn, 41.91 %; mol. wt., 852.)

Hydrogen polysulfide and di-n-butyldi-β-methallyltin

These compounds reacted to form $[(n\text{-}C_4H_9)_2SnS_{1.4}]_3$. (Found: C, 35.40; H, 6.27; S, 15.97; Sn, 42.27; mol. wt., 795. $C_{24}H_{54}Sn_3S_{4.2}$ calcd.: C, 34.53; H, 6.41; S, 16.19; Sn, 42.81 %; mol. wt., 834.)

Hydrogen polysulfide

Hydrogen polysulfide was prepared in accordance with the method of Mellor[8], using sodium tetrasulfide. Molecular weight determination indicated the average composition to be $H_2S_{5.2}$.

SUMMARY

A series of mono- and diallyl- and β-methallyltin compounds was treated with hydrogen polysulfide to form tin containing polysulfides. In each case, the course of the reaction was followed by infrared spectroscopy and the mode of addition determined.

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Short Communications

The preparation of organolithium compounds by the transmetalation reaction

IX*. Benzyllithium

Gilman and McNinch have described the preparation of benzyllithium by lithium metal cleavage of benzyl ethers[2] and have reviewed previous literature concerning the preparation of this reagent[2,3]. We felt that none of the available procedures for benzyllithium was wholly satisfactory and that a practical laboratory procedure for benzyl-

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* Part VIII: ref. 1.

lithium was needed. Benzyllithium has been prepared by the reaction of phenyllithium with benzyltriphenyltin in ether, but, although the tetraphenyltin yield was reported[4] to be *ca.* 90 %, the benzyllithium yield (established by carbonation) was only 39 %.

Our interest in applications of the organolithium–organotin transmetalation reaction prompted us to investigate if this procedure might not be applied more advantageously to the preparation of benzyllithium than the results of Gilman and Rosenberg suggest. We report here a procedure for benzyllithium based on the transmetalation reaction which we find serves excellently:

$$(C_6H_5CH_2)_3SnCl + 4CH_3Li \xrightarrow[\text{ether}]{\text{diethyl}} 3C_6H_5CH_2Li + (CH_3)_4Sn + LiCl \qquad (1)$$

There are several advantages to this procedure: (*1*) The starting material, tribenzyltin chloride, is easily accessible via the direct reaction of benzyl chloride with metallic tin in aqueous medium[5]. (2) The reaction itself gives benzyllithium in high yield. Determination of the yield by addition of trimethylchlorosilane to such a reaction mixture gave benzyltrimethylsilane in 89 % yield. (3) The organotin product, tetramethyltin, is low boiling (78°) and is removed easily with the solvent by distillation.

The use of phenyllithium in place of methyllithium in reaction (1) is not of advantage. In our hands complete consumption of phenyllithium was not obtained when the phenyllithium/tribenzyltin chloride ratio was 4. When trimethylchlorosilane was used to characterize the lithium reagents present, a mixture of benzyl- and phenyltrimethylsilane containing 5–8 % of the latter was obtained*. Special distillation equipment was required for their separation. When solubility factors in later steps were favorable, it was found that the phenyllithium procedure could give a pure product. Thus benzyltriphenylsilane was prepared in 62 % yield when triphenylchlorosilane was added to a benzyllithium solution prepared by the 4:1 phenyllithium/tribenzyltin chloride procedure[6]. The tetraphenylsilane which would have resulted if a small amount of phenyllithium had still been present when the triphenylchlorosilane was added is much less soluble in ether than benzyltriphenylsilane.

The metal displacement reaction also was investigated briefly; it appeared to offer no special advantage over the transmetalation reaction. The yield of benzyllithium (determined using trimethylchlorosilane) obtained was *ca.* 70 %, based on the following equation:

$$(C_6H_5CH_2)_3SnCl + 4Li \xrightarrow{\text{THF}} 3C_6H_5CH_2Li + LiCl + Sn,$$

when tribenzyltin chloride in tetrahydrofuran solution was treated with an excess of lithium dispersion.

Experimental

General comments. All reactions were carried out under an atmosphere of prepurified nitrogen. Methyl- and phenyllithium were prepared using standard procedures.

Preparation of benzyllithium: recommended procedure. In a 500 ml, three-necked flask equipped with a stirrer, reflux condenser and dropping funnel, and flushed previously with nitrogen, was placed 10.7 g (0.025 mole) of tribenzyltin chloride[5] and 100 ml of diethyl ether. To this mixture was added dropwise with stirring 68 ml of 0.146 *N* methyllithium in ether over 20 min; the resulting mixture was stirred at

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* Initial experiments were carried out in 1959–60 in these Laboratories by Mr. C. R. Sabet[6].

room temperature for 3.5 h. To the bright yellow ether solution (containing suspended white solid) was added 8.15 g (0.075 mole) of trimethylchlorosilane (Dow Corning Corp.), and the reaction mixture was stirred at room temperature overnight. It then was hydrolyzed with saturated ammonium chloride solution. The organic layer was separated and dried. Distillation gave first a mixture of ether and tetramethyltin, then benzyltrimethylsilane, b.p. 57–58° (8 mm), n_D^{25} 1.4908 (lit.[7] n_D^{25} 1.4909), 11.0 g (89.4 %). The g.l.c. retention time (General Electric SE-30 Silicone Gum on Chromosorb W, jacket temp. 190°, preheater temp. 195°, 15 p.s.i. helium) and the infrared spectrum of the product were identical to those of an authentic sample prepared by the Grignard procedure. Gas chromatographic analysis (Dow Corning 710 Silicone Fluid on Chromosorb W) of the ether–tetramethyltin distillate showed that the latter had been formed in 92 % yield.

Benzyllithium by metal displacement. In a 200 ml flask equipped as described above was placed 4.6 g of a dispersion of lithium (which contained 2 % sodium), 30 % by weight in hydrocarbon grease (Lithium Corp. of America). The hydrocarbon grease was washed away with two 100 ml portions of tetrahydrofuran (THF), and the lithium which remained was suspended in 30 ml of THF. To this suspension was added with stirring a solution of 8.55 g (0.02 mole) of tribenzyltin chloride in 70 ml of THF during 30 min. A slightly exothermic reaction was observed, and the color of the solution became greenish brown. The mixture was stirred at room temperature for 12 h. Trimethylchlorosilane (10.8 g, 0.1 mole) was added, and the reaction mixture was stirred overnight. It was hydrolyzed carefully with saturated ammonium chloride solution and filtered to give 1.8 g (76 %) of metallic tin. The organic layer was separated and the aqueous phase extracted with ether. The combined organic phases were dried and distilled to give 6.6 g (67 %) of benzyltrimethylsilane, n_D^{25} 1.4904. One g of waxy distillation residue remained.

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