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HALOMETHYL–METAL COMPOUNDS
XXII*. THE PREPARATION OF TRIHALOMETHYL AND OTHER HALOGENATED ORGANOTIN COMPOUNDS**

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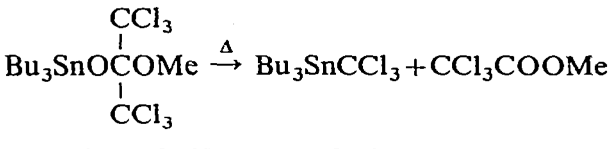
SUMMARY

The compounds Me_3SnCCl_3, Me_3SnCCl_2H, Me_3SnCCl_2Ph and Me_3SnCCl_2-Me have been prepared by reaction of the appropriate organolithium reagent with trimethyltin chloride at low temperature. The reaction of phenyl(bromodichloromethyl)mercury with trimethyltin bromide in refluxing benzene solution produced Me_3SnCCl_2Br in 63% yield. An experiment in which this mercury reagent was allowed to react with trimethyltin chloride gave both Me_3SnCCl_3 and Me_3SnCCl_2Br, which suggests that this route to trihalomethyl–tin compounds proceeds both by CCl_2 insertion into the Sn–X bond and by substituent exchange between mercury and tin.

INTRODUCTION

For an investigation of the possible general utility of trihalomethyl and other halogenated organotin compounds as potential carbene transfer reagents, compounds of type R_3SnCX_3 and R_3SnCX_2R' ($X = Cl$, Br) were required. At the time this work was initiated, (monohalomethyl)tin compounds were well-known[3], but the only (polyhalomethyl)tin derivative to have been prepared was trimethyl(trifluoromethyl)tin[4,5]. During the course of our work, however, other workers reported the preparation of (trihalomethyl)tin compounds by routes other than those used in the present investigation:



$$Bu_3SnO\overset{CCl_3}{\underset{CCl_3}{C}}OMe \xrightarrow{\Delta} Bu_3SnCCl_3 + CCl_3COOMe$$

(ref. 6)

$$R_3SnNR'_2 + HCX_3 \rightarrow R_3SnCX_3 + R'_2NH$$
$$(X = Cl, Br;\ R = Me, Bu;\ R' = Me, Et)$$

(ref. 7, 8)

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[*] Part XXI: ref. 1.

[**] Preliminary communication: ref. 2.

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RESULTS AND DISCUSSION

Most of our preparations of (α-polyhaloalkyl)tin compounds were accomplished using the organolithium route:

$$RCCl_2Li + Me_3SnX \rightarrow Me_3SnCCl_2R + LiX$$
$$(R = Cl,\ H,\ CH_3,\ Ph)$$

This was made possible by the development of useful synthetic polyhaloalkyllithium chemistry by several groups in recent years[9-11]. (For a review of this area, see ref. 12.) The most notable feature of the preparation and utilization of polyhaloalkyllithium reagents is the fact that they are stable only at low (−60° to −120°) temperatures. Tetrahydrofuran has been found to stabilize such lithium reagents (compared to diethyl ether), but systems containing only THF as solvent tend to freeze at −100° even when vigorously stirred. Köbrich and coworkers[11,13] used a solvent system containing THF, diethyl ether and pentane in 4/1/1 volume ratio with good success, and another system, THF, pentane, diethyl ether and methylal (dimethoxymethane), also has been employed for low temperature organolithium work[14]. We have made extensive use of these solvent systems, but during the later stages of the present study we developed still another solvent system for low temperature organolithium synthesis and reactions: 3/1 by volume THF/dimethyl ether. It is, in our opinion, superior to the other systems in terms of ease of formulation, low viscosity and low freezing point. Only one solvent, THF, requires prior purification by drying and distillation. Gaseous (b.p. −23.7°) dimethyl ether was prepared for use simply by passing it through a drying tower containing activated alumina, anhydrous calcium sulfate and phosphorus pentoxide and condensing it in a cold trap.

The preparation of trimethyl(trichloromethyl)tin in 62% yield was accomplished by quenching a solution of trichloromethyllithium[13] at −100° in Köbrich's solvent system with an equimolar amount of trimethyltin chloride. The extremely labile $Cl_3C{-}Sn$ bond made isolation and purification of this compound difficult. Trimethyl(trichloromethyl)tin is very moisture-sensitive; small samples hydrolyze rapidly and quantitatively to trimethyltin hydroxide and chloroform when exposed to atmospheric moisture. The compound sublimes readily but it decomposed when distillation was attempted. The usual methods for separating unconverted trimethyltin chloride from Me_3SnR preparations failed: alcoholic potassium fluoride and anhydrous ammonia in diethyl ether also destroyed trimethyl(trichloromethyl)tin. The lithium chloride formed in the coupling reaction interfered in the purification of trimethyl(trichloromethyl)tin and had to be removed by a nonaqueous procedure, precipitation with 1,4-dioxane. It is clear that where it is applicable, the $Me_3SnNR_2/RCHCl_2$ procedure[7,8] is preferable to the organolithium route.

(α,α-Dichlorobenzyl)trimethyltin, a distillable liquid prepared in 53% yield via α,α-dichlorobenzyllithium[10,13], appeared to be sensitive to both moisture and oxygen, the slightest exposure to the atmosphere immediately producing a yellow coloration. 1,1-Dichloroethyllithium, a new reagent prepared by reaction of n-butyllithium with 1,1-dichloroethane at −115°, was used to prepare trimethyl(1,1-dichloroethyl)tin (49%), a volatile, moisture-sensitive solid. Trimethyl(dichloromethyl)tin, a distillable liquid which was stable to atmospheric moisture, was obtained in 66%

yield by reaction of dichloromethyllithium[11,15] with trimethyltin chloride. Subsequently, (dichloromethyl)tin compounds were prepared by other workers using two different procedures: insertion of sodium trichloroacetate-derived dichlorocarbene into the Sn–H bond of triethyl- and tri-n-butyltin hydride[16] and reduction of trialkyl(trichloromethyl)tin compounds with organotin hydrides[17].

The discovery in these Laboratories that dihalocarbenes will insert into the mercury–halogen linkage[18] suggested to us that a similar route might be preparatively useful for (trihalomethyl)tin compounds. We had our first indication that CX_2 insertion into the tin–halogen bond could occur during the organolithium work referred to above. It was found that the reaction of trimethyltin bromide with trichloromethyllithium at −100° gave not only Me_3SnCCl_3 but also an equal amount of a second trimethyltin compound which was moisture-sensitive, had a similar IR spectrum and which tentatively was identified as trimethyl(bromodichloromethyl)tin. This compound might have arisen from insertion of lithium chloride-complexed dichlorocarbene (produced upon warming the reaction mixture containing unreacted trichloromethyllithium) into the Sn–Br bond of trimethyltin bromide.

The thermolysis of phenyl(bromodichloromethyl)mercury, an excellent dichlorocarbene source[19], in the presence of trimethyltin bromide (50% excess) in refluxing benzene solution did indeed produce the desired trimethyl(bromodichloromethyl)tin in 63% yield. The presence of unconverted trimethyltin bromide rendered the isolation of this product quite difficult; preparative GLPC with a specially designed cell-bypass was required to achieve separation. The IR spectrum of the product was identical with that of the by-product of the CCl_3Li/Me_3SnBr reaction, thus confirming that the latter was Me_3SnCCl_2Br.

While the premise upon which our $PhHgCCl_2Br/Me_3SnBr$ experiment was based was that mercurial-derived dichlorocarbene should be capable of inserting into the Sn–Br bond, another mechanism for this Me_3SnCCl_2Br-producing reaction was possible: substituent exchange between tin and mercury, in which the intact CCl_2Br moiety is transferred from mercury to tin. In order to obtain information concerning the mechanism of this reaction, the analogous reaction of phenyl(bromodichloromethyl)mercury and trimethyltin *chloride* was examined. In this case, the insertion process should give trimethyl(trichloromethyl)tin (in the absence of complicating halogen exchange reactions) and the substituent exchange process should give trimethyl(bromodichloromethyl)tin. When this reaction was carried out, the total product yield was only 16%, probably as a result of a lesser reactivity of the Sn–Cl bond. However, the important fact which emerged upon GLPC analysis of the reaction mixture was that a 1.5/1 mixture of Me_3SnCCl_3 and Me_3SnCCl_2Br had been formed. A possible explanation for this result, the formation of trimethyltin bromide by reaction of phenylmercuric bromide with trimethyltin chloride (then followed by CCl_2 insertion into the Sn–Br bond) was excluded by experiment. From these results it would appear that trimethyl(bromodichloromethyl)tin could have been formed by both possible routes in the $PhHgCCl_2Br/Me_3SnBr$ reaction. The preparation of tri-n-butyl(trichloromethyl)tin by Chinese workers via reaction of dichlorocarbene with tri-n-butyltin chloride has been alluded to in ref. 7, but no details of this work are available to us.

The availability of Me_3SnCCl_3, Me_3SnCCl_2Br, Me_3SnCCl_2H, Me_3SnCCl_2Ph and of the compounds $Me_3SnCX_2SnMe_3$ (X = Cl, Br)[20] has made possible the study of (α-polyhaloalkyl)tin compounds as divalent carbon transfer agents, and the results of this investigation will be presented in a later paper of this series.

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of prepurified nitrogen or argon. Methyltin compounds were obtained from M&T Chemicals, Inc., n-butyllithium from the Foote Mineral Co. Phenyl(bromodichloromethyl)mercury was prepared as described by us previously, either in benzene medium[21] or in diethyl ether[22]. (Note, however, our improved procedure for this mercurial[23].) Elemental analyses were performed by Dr. S. M. Nagy (M.I.T.) and by the Galbraith Laboratories, Knoxville, Tennessee. IR spectra were recorded using a Perkin–Elmer 337 grating spectrophotometer, NMR spectra with a Varian Associates A60 NMR spectrometer. Chemical shifts are given in ppm downfield from internal TMS.

The low temperature organolithium reactions were carried out in a three-necked Morton (creased) flask (usually a 500 ml flask) equipped with a high speed stirrer, pressure-equalizing dropping funnel, pentane thermometer (or thermocouple connected to a recorder) and a gas inlet tube. Of the solvents used, THF was purified by distillation from lithium aluminum hydride, diethyl ether and pentane from calcium hydride, methylal from lithium aluminum hydride.

Trimethyl(trichloromethyl)tin

Into the 500 ml reaction flask (*cf.* section above) was placed 13.85 g (0.115 mole) of chloroform (dried over calcium chloride and passed through Woelm neutral activated alumina immediately before use) and 240 ml of a 4/1/1 mixture of THF, diethyl ether and pentane under an atmosphere of dry nitrogen. The solution was cooled to −100° and then 72.3 ml (0.112 mole) of 1.55 *N* n-butyllithium in hexane was added with stirring over a 1 h period. After an additional 2 h period of vigorous stirring, 19.84 g (0.10 mole) of trimethyltin chloride in ether was added over a 25 min period. The mixture was stirred at −100° for 2 h, then was allowed to warm to room temperature. Fifty ml of 1,4-dioxane was added to precipitate the lithium halide; the 7.3 g of whitish-brown solid thus obtained was filtered under nitrogen and the filtrate was concentrated at 60 mm using a rotary evaporator. The residue was trap-to-trap distilled at 0.01 mm (70° pot temperature). Two fractions were taken; the second was collected when sublimed solid began to appear on the cooler surfaces of the apparatus and it was essentially pure trimethyl(trichloromethyl)-tin, 17.92 g (62%). Its m.p. after recrystallization from pentane at −80° was 61–63° (sintering at 40–42°). Davies and Mitchell[7] reported a m.p. of 54–59°; Chivers[8] reported 41–42°. (Found: C, 17.05; H, 3.62. $C_4H_9Cl_3Sn$ calcd.: C, 17.00; H, 3.22%.) NMR (in CS_2): singlet at 0.50 ppm [$J(^{117}Sn-^{1}H)$ 51 cps; $J(^{119}Sn-^{1}H)$ 55 cps]. IR spectrum (in CS_2): 2985 m; 2915 m; 1380 m; 1193 (sh); 775 vs; 698 vs; 642 (sh); 583 s, cm^{-1}.

Exposure of a small sample of the product to atmospheric moisture gave trimethyltin hydroxide, m.p. 116–118° (lit.[24] m.p. 118°). Cleavage of another sample with an excess of bromine gave methyl bromide, bromotrichloromethane and tin tetrabromide.

Trimethyl(dichloromethyl)tin

Dichloromethyllithium was prepared at −100° under nitrogen from 10.04 g (0.118 mole) of dichloromethane and 0.112 mole of n-butyllithium solution in 245 ml of the THF/diethyl ether/pentane mixture. To this solution was added with stirring at −100° 20.12 g (0.101 mole) of trimethyltin chloride over a 20 min period. The reaction mixture was stirred for 2 h at −100°, warmed to room temperature, treated with 50 ml of dioxane and filtered from 29.56 g of white solid. Solvents were removed from the filtrate at reduced pressure and the residue was trap-to-trap distilled at 0.02 mm (room temperature) to give 23.00 g of clear liquid. Redistillation through a 12″ Vigreux column gave 16.40 g (66%) of trimethyl(dichloromethyl)tin, b.p. 86–87° (38 mm), n_D^{25} 1.5030. (Found: C, 19.34; H, 4.04; Cl, 29.00; Sn, 47.51. $C_4H_{10}Cl_2Sn$ calcd.: C, 19.39; H, 4.07; Cl, 28.62; Sn, 47.92%.) NMR spectrum (in CCl_4): singlets at 0.3 ppm [$J(^{117}Sn-^{1}H)$ 53.5 cps; $J(^{119}Sn-^{1}H)$ 56.5 cps] and at 5.4 ppm [$J(Sn-H)$ 15 cps]. IR spectrum (liquid film): 2980 m; 2910 m; 2340 w; 1480 w; 1410 w; 1198 (sh); 1194 m; 1095 w; 778 vs; 725 m; 688 vs; 540 vs, cm^{-1}.

(α,α-Dichlorobenzyl)trimethyltin

α,α-Dichlorobenzyllithium was prepared at −100° by reaction of 20.16 g (0.10 mole) of benzotrichloride and 0.10 mole of n-butyllithium solution in a solvent mixture of 180 ml of THF and 60 ml of dimethyl ether (purified as mentioned in the discussion section). During the course of the addition, during which the mixture gradually turned deep red, the temperature was lowered to below −120°. After the reagent solution had been stirred at this temperature for 30 min, 19.64 g (0.099 mole) of trimethyltin chloride in 6 ml of ether was added. A change in color to light orange resulted. The reaction mixture was stirred for 95 min at low temperature, then was warmed to room temperature, treated with 50 ml of dioxane and filtered to remove 11.75 g of white solid. The filtrate was concentrated at 15 mm and the residue trap-to-trap distilled at 0.05 mm. The first fraction (no external heating) was discarded; the second fraction (pot temperature to 120°) was redistilled (*acid-washed* short path distillation unit) to give 16.80 g (53%) of product, b.p. 77–80° (0.06 mm). (α,α-Dichlorobenzyl)trimethyltin, a colorless liquid when freshly distilled, was extremely sensitive to moisture and apparently also to oxygen. (Found: C, 36.99; H, 4.21; Sn, 36.39. $C_{10}H_{14}Cl_2Sn$ calcd.: C, 37.09; H, 4.36; Sn, 36.66%.) NMR spectrum (in CCl_4): singlet at 0.25 ppm [$J(^{117}Sn-^{1}H)$ 52 cps; $J(^{119}Sn-^{1}H)$ 54 cps]; multiplet at 6.80 to 7.40 ppm. IR spectrum (in CCl_4): 3080 (sh); 3060 m; 3030 (sh); 3005 (sh); 2985 m; 2910 m; 2350 w; 1950 w; 1880 w; 1770 m; 1730 w; 1680 (sh); 1650 w; 1590 m; 1485 s; 1465 w; 1445 s; 1385 (sh); 1380 w; 1325 (sh); 1312 w; 1226 w; 1205 (sh); 1195 m; 1178 w; 1078 w; 1035 m; 998 w; 913 w; 871 w; 845 w; 830–730 (obscured by solvent); 708 vs; 690 vs; 668 (sh); 645 (sh); 615 (sh); 605 m; 533 vs, cm^{-1}.

Trimethyl(1,1-dichloroethyl)tin

1,1-Dichloroethyllithium was prepared at −115° from 5.00 g (50.5 mmoles) of 1,1-dichloroethane and 49.6 mmoles of n-butyllithium solution in 98 ml of 3/2/1/1 THF/diethyl ether/pentane/methylal mixture. The reagent solution was stirred at −115° for 2 h and then 9.65 g (46.3 mmoles) of trimethyltin chloride was added. The reaction mixture was stirred at −115° for 1.5 h, warmed to room temperature, treated with 10 ml of dioxane and filtered. The filtrate was trap-to-trap distilled at 0.02 mm to give a solvent fraction at room temperature and another fraction (heating with a heat lamp), 25.23 g, shown by gas chromatography (General Electric Co. SE-30 silicone rubber gum on Chromosorb P at 80–185°; tetralin internal standard; F&M 700 instrument) to contain solvent, trimethyltin chloride, n-butyltrimethyltin (20% yield) and trimethyl(1,1-dichloroethyl)tin (49% yield). An analytical sample of the latter, a crystalline solid, m.p. 58–59° (sealed tube) was collected by GLPC. (Found: C, 23.26; H, 4.86; Cl, 27.38. $C_5H_{12}Cl_2Sn$ calcd.: C, 22.94; H, 4.62; Cl, 27.09%) NMR spectrum (in chloroform): singlets at 0.36 ppm [$J(^{117}Sn-^{1}H)$ 53.5 cps; $J(^{119}Sn-^{1}H)$ 56 cps] and at 2.20 ppm [$J(^{117}Sn-^{1}H)$ 35 cps; $J(^{119}Sn-^{1}H)$ 37 cps] in an area ratio of 3/1. IR spectrum (in CS_2): 2970 s; 2955 s; 2905 s; 2840 m; 2350 m; 1720 w; 1695 w; 1440 s (in $CHCl_3$); 1430 s (in $CHCl_3$); 1365 s; 1104 w; 1057 s; 1020 s; 775 vs; 719 (sh); 695 s; 642 vs; 530 s, cm^{-1}.

Trimethyl(bromodichloromethyl)tin

Into a dried 500 ml, three-necked flask equipped with magnetic stirring unit, reflux condenser and gas inlet tube, under an atmosphere of dry nitrogen was placed 44.04 g (0.10 mole) of phenyl(bromodichloromethyl)mercury, 37.40 g (0.154 mole) of trimethyltin bromide and 250 ml of benzene (freshly distilled from calcium hydride). The solution was heated at reflux and stirred for 3 h. The phenylmercuric bromide which precipitated, 33.75 g (95%), m.p. 284–287°, was filtered off under nitrogen. The filtrate was concentrated at 20 mm on a rotary evaporator and the residue was trap-to-trap distilled at 0.02 mm (pot temperature to 70°). Analysis of the distillate by GLPC (20% SE-30 on Chromosorb P; M.I.T. isothermal unit, 70° column temperature, benzotrichloride internal standard) showed the presence of trimethyl(bromodichloromethyl)tin in 63% yield and of tetrachloroethylene in 17% yield. Analytical and preparative samples of the product, a white, crystalline solid, m.p. (sealed tube) 103.5–105°, were isolated by GLPC using a cell by-pass system (described in the thesis of F.M.A., M.I.T., 1968). (Found C, 14.77; H, 3.05; AgX, 9.040 mg from a 6.805 mg sample. $C_4H_9Cl_2BrSn$ calcd.: C, 14.69; H, 2.77%; AgX, 9.079 mg.) NMR spectrum (in CS_2): singlet at 0.49 ppm [$J(^{117}Sn-^{1}H)$ 52 cps; $J(^{119}Sn-^{1}H)$ 55 cps]. IR spectrum (in CS_2): 2980 m; 2915 m; 1385 m; 1193 s; 778 vs; 700 vs; 641 vs; 534 vs, cm^{-1}.

A small sample gave trimethyltin hydroxide (m.p. 114°) and bromodichloromethane (identified by GLPC retention time) when exposed to the atmosphere. Cleavage of another sample with an excess of bromine gave methyl bromide, dibromodichloromethane and tin tetrabromide.

Reaction of phenyl(bromodichloromethyl)mercury with trimethyltin chloride.

A similar reaction was carried out using 10.0 mmoles each of the mercurial and trimethyltin chloride and 25 ml of benzene. The reaction mixture was stirred at reflux for 3 h. Phenylmercuric bromide, 2.34 g (66% yield), was removed by filtration. GLPC analysis of the filtrate (SE-30; benzotrichloride internal standard) showed that trimethyl(trichloromethyl)tin (9.4%) and trimethyl(bromodichloromethyl)tin (6.6%) had been produced. The products were identified by comparison of their GLPC retention times and their IR spectra with those of authentic samples.

In a similar experiment (8 h reflux period), the yields of the (trichloromethyl)- and (bromodichloromethyl)tin compounds were 11% and 4.8%, respectively.

Reaction of phenyl(trichloromethyl)mercury with trimethyltin chloride

Using the general procedure described above, a reaction was carried out between 19.7 mmoles of trimethyltin chloride and 30 mmoles of phenyl(trichloromethyl)-mercury in 50 ml of benzene, at 80° for 80 h. Phenylmercuric chloride (4.12 g, 66%) was filtered off, the filtrate was concentrated at reduced pressure and the residue trap-to-trap distilled at 0.02 mm. A moist, crystalline solid was thus obtained (1.92 g). Its analysis by GLPC showed the presence of trimethyl(trichloromethyl)tin in 6.4% yield. The product was identified by means of its GLPC retention time and its IR spectrum. A distillation residue of 3.53 g remained.

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