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

CHLOROCARBON DERIVATIVES OF TIN*

T. CHIVERS** AND B. DAVID
The Chemical Laboratory, University of Sussex, Brighton, Sussex (Great Britain)

(Received January 10th, 1968)

SUMMARY

Me_3SnCCl_3 (II) and $Me_3SnCCl{=}CCl_2$ (III) have been obtained by the reaction of (dimethylamino)trimethyltin (I) with the appropriate chlorohydrocarbon. $Me_3SnC_6Cl_5$ (IV) has been prepared from trimethyltin chloride and either C_6Cl_5Li or C_6Cl_5MgCl. (Trichloromethyl)trimethyltin with BCl_3 at 25° gives $Me_2Sn(CCl_3)Cl$ (V), which on treatment with BCl_3 at 60° gives Me_2SnCl_2. Dimethyl(trichloromethyl)tin chloride gives Me_2SnCl_2 when heated at 120°, and when heated with water at 60° 1,3-dichloro-1,1,3,3-tetramethyldistannoxane is obtained.

On treatment with aqueous alcoholic solutions of fluoride ion or alcoholic base (pentachlorophenyl)trimethyltin loses pentachlorophenyl as C_6Cl_5H. The reaction of $Me_3SnC_6Cl_5$ with BCl_3 at 100° gives (pentachlorophenyl)boron dichloride (VI). Thermal decomposition of (pentachlorophenyl)trimethyltin at 30° gives Me_3SnCl in 87% yield. Alternative mechanisms for the thermal decomposition of (IV) are discussed, and the possibility of intramolecular Sn–Cl coordination in (IV) is suggested.

INTRODUCTION

Recent publications indicate that there is current interest in chlorocarbon derivatives. Trichloromethylmagnesium[1] and -lithium[2-4] reagents have been synthesised, and the latter has been used to prepare trichloromethyl derivatives of mercury[4], silicon[5] and tin[6]. The mercurials have been shown to act as excellent carbene transfer reagents[7]. Other synthetic routes have led to trichloromethyl derivatives of silicon[8,9], mercury[10], tin[11,12], lead[13,14], and phosphorus[15]. That hexachlorobenzene forms a Grignard reagent with magnesium in THF has been known for some time[16], and pentachlorophenyllithium has recently been synthesised by direct metalation[17] and by metal–halogen exchange[18]. These reagents have been used to prepare pentachlorophenyl derivatives of mercury[19,20], silicon[18,21], tin[22], phosphorus[18], cobalt[18,23] and nickel[18,23].

The present work describes the synthesis and some reactions of chlorocarbon derivatives of tin of the type Me_3SnR_{Cl}, (where $R_{Cl} = CCl_3$, $CCl{=}CCl_2$, or C_6Cl_5).

This work was undertaken in order to compare the reactions of chlorocarbon-tin compounds with their fluorocarbon analogues, and to probe the nature and extent of tin–chlorine interactions, if any, in such derivatives.

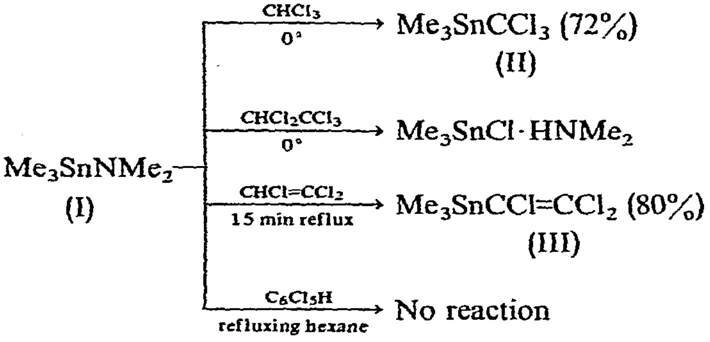
---

* For a preliminary communication: see ref. 42.

** Present address: Department of Chemistry, The University of British Columbia, Vancouver 8 (Canada).

RESULTS AND DISCUSSION

The preparation of (trichloromethyl)trimethyltin by the reaction of chloroform with (diethylamino)trimethyltin has been demonstrated by Davies and Mitchell[11]. By employing other chlorohydrocarbons, we have sought to extend this route to chlorocarbon–tin derivatives. The results are shown below.



When an excess of chloroform is added to (dimethylamino)trimethyltin (I) at 0°, reaction takes place smoothly to give good yields of (trichloromethyl)trimethyltin (II). However, with pentachloroethane at 0°, the dimethylamine adduct of trimethyltin chloride is obtained. This appears to be another example of a dehydrochlorination reaction of (I). Such behaviour has recently been observed by Cardin and Lappert[24]. The elimination of HCl from pentachloroethane may involve a concerted multicentre pathway. Alternatively, formation of (pentachloroethyl)trimethyltin, $Me_3SnC_2Cl_5$, may occur, followed by β-chlorine migration to tin to give trimethyltin chloride, which in the presence of liberated dimethylamine would give the observed adduct.

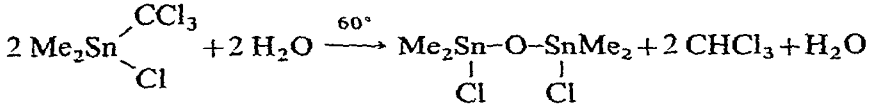
Trichloroethylene with (I) gives a high yield of (trichlorovinyl)trimethyltin (III), after short periods at reflux. Trichlorovinyl derivatives of silicon and germanium have been obtained by the reaction of phenyl(bromodichloromethyl)mercury with bis(trimethylsilyl)mercury and bis(trimethylgermyl)mercury, respectively[41], but trichlorovinyl derivatives of tin were hitherto unknown. Pentachlorobenzene was unreactive towards (I), even in refluxing hexane, but (pentachlorophenyl)trimethyltin (IV), can be obtained in good yields by treatment of trimethyltin chloride with pentachlorophenyllithium in diethyl ether or pentachlorophenylmagnesium chloride in THF.

The reaction between (trichloromethyl)trimethyltin and boron trichloride at 25° in a sealed tube causes cleavage of a methyl group from tin to occur to give (trichloromethyl)dimethyltin chloride (V).

$$Me_3SnCCl_3 + BCl_3 \rightarrow \underset{(V)}{Me_2(CCl_3)SnCl} + MeBCl_2$$

The analogous (trifluoromethyl)tin compound $Me_2(CF_3)SnCl$, has been prepared by the action of chlorine on (trifluoromethyl)trimethyltin[25]. The cleavage of a methyl group from tin in preference to a trichloromethyl group by the electrophilic reagent boron trichloride is consistent with previous work by Kaesz, Stafford and Stone with mixed alkylperfluoroalkyltin derivatives[26]. Because of the inductive effect of the chlorine atoms, the electron density at the carbon atom of the trichloromethyl group will be less than that at the carbon atom of the unsubstituted methyl group. Consequently, electrophilic attack will occur at the unsubstituted carbon atom. In view of this, it is noteworthy that Davies *et al.*, have reported that in reactions with bromine[11] and hydrogen chloride[12], (trichloromethyl)trialkyltins release a trichloromethyl group.

Reaction of (V) with another mole of boron trichloride cleaves a trichloromethyl group from tin to give dimethyltin dichloride. (Trichloromethyl)dimethyltin chloride shows limited thermal stability. For example, after 16 h at 72° it was recovered in 73% yield, but at 120° considerable decomposition occurred to give dimethyltin dichloride. (Trichloromethyl)dimethyltin chloride shows a marked enhancement of stability towards atmospheric hydrolysis when compared to (II). Whereas (II) is rapidly converted to trimethyltin hydroxide and chloroform on exposure to moist air[6], (V) is unchanged under similar conditions. When heated in a sealed tube with water at 60°, however, hydrolysis does occur to give 1,3-dichloro-1,1,3,3,-tetramethyldistannoxane and chloroform.



$$2\,\mathrm{Me_2Sn}\overset{\mathrm{CCl_3}}{\underset{\mathrm{Cl}}{}} + 2\,\mathrm{H_2O} \xrightarrow{60^\circ} \underset{\mathrm{Cl}}{\mathrm{Me_2Sn}}\text{–O–}\underset{\mathrm{Cl}}{\mathrm{SnMe_2}} + 2\,\mathrm{CHCl_3} + \mathrm{H_2O}$$

(Pentachlorophenyl)trimethyltin (IV) can be prepared in 46% yield by the reaction between trimethyltin chloride and pentachlorophenylmagnesium chloride in THF at reflux. Better yields may be obtained by using pentachlorophenyllithium in diethyl ether at −10°. (Pentachlorophenyl)trimethyltin is a white crystalline solid which may be recrystallised from aqueous ethanol. However, when (IV) is refluxed for 10 min in aqueous ethanolic solution containing a trace of fluoride ion, pentachlorobenzene is obtained in 90% yield.

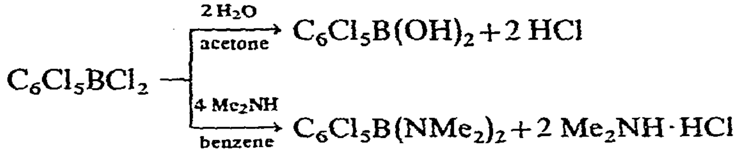
$$\mathrm{Me_3SnC_6Cl_5} \xrightarrow[\text{reflux}]{\mathrm{F^-/EtOH/H_2O}} \mathrm{C_6Cl_5H} + \mathrm{Me_3SnOH}\,.$$

This is apparently another example of nucleophilic-assisted solvolysis of an aryl–tin bond, which has previously been reported for (pentafluorophenyl)tin compounds[27]. Cleavage of (IV) by alcoholic base occurs readily at room temperature to give pentachlorobenzene in high yield. Similar behaviour has been reported for (pentachlorophenyl)silanes[22].

Electrophilic cleavage of (IV) with boron trichloride at 100° gives (pentachlorophenyl)boron dichloride (VI).

$$\underset{\text{(IV)}}{\mathrm{Me_3SnC_6Cl_5}} + 2\,\mathrm{BCl_3} \xrightarrow[\text{sealed tube}]{100^\circ} \mathrm{Me_2SnCl_2} + \underset{\text{(VI)}}{\mathrm{C_6Cl_5BCl_2}} + \mathrm{MeBCl_2}$$

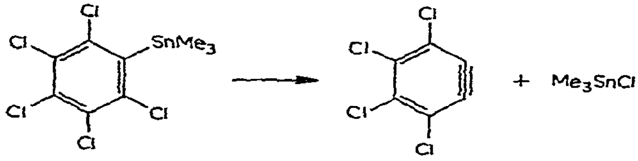
(Pentachlorophenyl)boron dichloride may readily be purified by sublimation (100°/10^{-2} mm) after removal of dimethyltin dichloride at (25°/10^{-2} mm). (Pentachlorophenyl)boron dichloride is a crystalline solid which gives off fumes of hydrogen chloride on exposure to the atmosphere. Hydrolysis of (VI) in aqueous acetone gives the corresponding boronic acid, $C_6Cl_5B(OH)_2$, and reaction with excess of dimethylamine in benzene gives bis(dimethylamino)(pentachlorophenyl)borane.



$$C_6Cl_5BCl_2 \begin{cases} \xrightarrow[\text{acetone}]{2\,H_2O} C_6Cl_5B(OH)_2 + 2\,HCl \\ \xrightarrow[\text{benzene}]{4\,Me_2NH} C_6Cl_5B(NMe_2)_2 + 2\,Me_2NH\cdot HCl \end{cases}$$

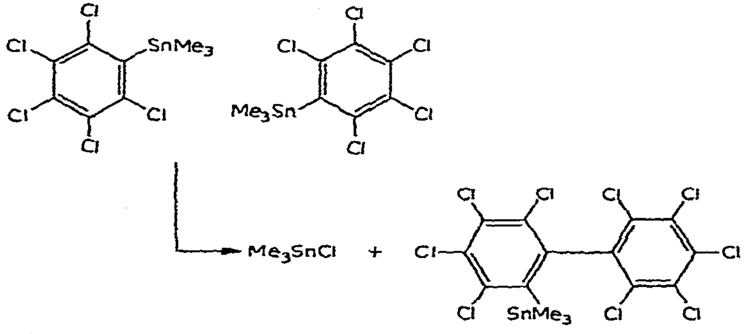
In contrast to (pentafluorophenyl)boron dichloride which undergoes disproportionation on heating at 220°[28], (pentachlorophenyl)boron dichloride can be recovered almost quantitatively after 20 h at 260°.

Seyferth and Evnin have reported that (2,3,4,5-tetrachlorophenyl)trimethyltin undergoes redistribution to give tetramethyltin and dimethylbis(2,3,4,5-tetrachlorophenyl)tin when heated at 230°. We find that the thermal decomposition of (IV) at 300° for 4 h gives trimethyltin chloride in 87% yield. The only other isolable product was a small amount of chlorocarbon whose analysis showed the C : Cl ratio to be 5.9 : 4. Intramolecular elimination of Me_3SnCl from (IV) might be expected to give tetrachlorobenzyne as an intermediate.



Attempts by us to trap this intermediate by causing decomposition to take place in mesitylene[30] have been unsuccessful.

A bimolecular route to decomposition is also possible.



(VII)

To account for the high yield of trimethyltin chloride from the thermal decomposition, elimination of trimethyltin chloride from (VII) must also occur. Under the reaction conditions this is quite possible, and it could clearly occur by a variety of routes which would give rise to a complexity of chlorocarbon products. Such behaviour has previously been reported for (iodoaryl)tin compounds[29].

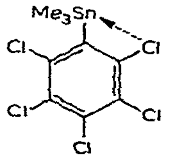
Ballester[31] *et al.*, have found that the UV spectra of polychloroaromatic derivatives having a $-CCl_3$ group flanked by two chlorine atoms show large bathochromic shifts when compared to pentachloro- or hexachlorobenzene. These results were interpreted in terms of molecular distortion due to interaction between the -CCl_3 group and *o*-chlorine atoms. We have recorded the UV spectra of $Me_3SiC_6Cl_5$ in cyclohexane (see Table 1) and observe a small bathochromic shift for the silicon derivative, but no significant shift for the tin compound. We conclude that molecular distortion in (IV) is negligible and this is understandable in terms of the large size of tin which would minimise interactions between *o*-chlorine atoms and methyl groups. In view of the thermally induced elimination of trimethyltin chloride from (IV), it is interesting to consider the possibility of intramolecular Sn–Cl coordination in (IV).

TABLE 1

UV SPECTRA OF PENTACHLOROPHENYL DERIVATIVES[a]

Compound	λ_{max}	$\varepsilon \times 10^{-3}$
C_6Cl_5H[b]	298	0.39
	289	0.37
C_6Cl_6[b]	298	0.23
	291	0.25
$C_6Cl_5SiMe_3$	306	0.66
	296	0.55
$C_6Cl_5SnMe_3$	301	0.39
	292	0.37
$C_6Cl_5CCl_3$[b]	319	1.42

[a] In cyclohexane. [b] Reference 31.



(IV)

Assuming normal bond angles and bond lengths (from covalent radii)[32] in (IV), calculation gives a value of 3.3 Å for the Sn to *o*-Cl distance in (IV). This compares with 3.8 Å for the sum of the Van der Waal's radii of tin and chlorine[33], and 2.3–2.4 Å for Sn–Cl bond lengths in alkyltin chlorides[34]. It is suggested therefore, that significant tin–chlorine interaction in (IV) may occur, particularly in view of the well-documented tendency of organotin compounds to achieve penta- or even hexa-coordination[35]. Studies aimed at elucidating the nature and extent of this interaction are in progress. The formation of penta- or hexa-coordinated species by intramolecular coordination has been postulated by Gilman and Sim to account for the high molar absorptivities shown by the 220 mμ band in the ultraviolet spectra of (pentachlorophenyl)silanes and -stannanes[22].

NQR studies with bis(pentachlorophenyl)mercury have been interpreted in terms of intramolecular coordination between *o*-chlorine atoms and mercury[36].

EXPERIMENTAL

General

An atmosphere of dry nitrogen was used for the preparation and handling of air-sensitive materials. Chlorohydrocarbons were stored over P_2O_5, and distilled from fresh P_2O_5 before use. Ether solvents were distilled from lithium aluminum hydride before use. (Dimethylamino)trimethyltin was prepared according to the method of Jones and Lappert[37]. (Pentachlorophenyl)trimethylsilane was prepared by the method of Rausch *et al.*[18]. IR spectra were obtained with a Perkin–Elmer Model 237 Infracord using sodium chloride plates. NMR spectra were obtained with a Varian HA100 spectrometer. UV spectra were recorded on a Unicam SP 800B Spectrophotometer. Analyses were performed by A. Bernhardt, Mülheim, Ruhr, and by the microanalytical laboratory at the University of Sussex.

Preparation of chlorocarbon–tin compounds

(Trichloromethyl)trimethyltin. An excess of chloroform was added dropwise to (dimethylamino)trimethyltin (4.71 g, 0.22 mole) which was cooled in an ice-bath. The reactants were allowed to stand at 0° for 15 min, and then excess of chloroform and dimethylamine were removed by vacuum transfer to give (trichloromethyl)trimethyltin (4.61 g, 0.16 mole, 72%) as a white powder m.p. 43–45° [lit.[11]: sintered at 43–45°, m.p. 54–59° (decompn.)].

The IR spectrum (Nujol) showed bands at 1220 w, 1200 m, 780 s, 765 s and 710 s cm^{-1}.

(Trichlorovinyl)trimethyltin. An excess of trichloroethylene was added dropwise to (dimethylamino)trimethyltin (1.60 g, 80 mmoles) at 0°. The reaction mixture was refluxed for 15 min. Excess of trichloroethylene was removed *in vacuo* to give a pale yellow liquid residue of (trichlorovinyl)trimethyltin (1.35 g, 65 mmoles, 80%), which was shown to be >95% pure by vapour phase chromatography. The b.p. was 111°/20 mm. An analytical sample was purified by VPC. (Found.: C, 20.60; H, 3.15. $C_5H_9Cl_3Sn$ calcd.: C, 20.42; H, 3.08%.)

The IR spectrum (liq. film) showed bands at 3000 m, 2930 m, 2380 w, 1540 s, 1400 w, 1265 w, 1200 m, 934 s, 835 s, 786 s, 735 s and 697 cm^{-1}. The band at 1540 s cm^{-1} is attributable to C=C stretching vibration and is close to that observed for trichlorovinyl-mercurials[38].

(Pentachlorophenyl)trimethyltin from C_6Cl_5MgCl. The Grignard reagent was prepared according to the method of Paulik *et al.*[19], from hexachlorobenzene (40 g, 0.14 mole) and magnesium (4.4 g, 0.18 mole) in THF (300 ml). The Grignard solution was decanted from unreacted magnesium and trimethyltin chloride (20 g, 0.10 mole) in THF (50 ml) was added dropwise to the solution. The reaction mixture was stirred at its ambient temperature for 1½ h and then at reflux for 4 h. On cooling, solvent was removed *in vacuo* and the brown solid residue was extracted with hot hexane (3 × 100 ml) to give a yellow solid (38 g), which after sublimation (130°/0.01 mm) and recrystallisation from ethanol gave white needles of (pentachlorophenyl)trimethyltin (19 g, 46%) which had m.p. 119–120° (Found: C, 26.01; H, 2.21; Cl, 42.83. $C_9H_9Cl_5Sn$ calcd.: C, 26.17; H, 2.20; Cl, 42.72%.) A sample of (pentachlorophenyl)trimethyltin stored in a stoppered bottle for several weeks was found to contain pentachlorobenzene. The compound should be stored in a dry atmosphere to avoid atmospheric hydrolysis.

The IR spectrum (Nujol) showed bands at 1345 m, 1329 s, 1305 s, 1172 w, 1084 w, 841 s, 783 s, 720 w and 670 s cm^{-1}. The ^{1}H NMR spectrum (in CCl_4 at 30°) showed a singlet at τ 9.45 (Sn-Me) with $J(^{119}\text{Sn–Me})$ 56.8, $J(^{117}\text{Sn–Me})$ 54.5 c/sec.

(Pentachlorophenyl)trimethyltin from C_6Cl_5Li. Trimethyltin chloride (10 g, 0.05 mole) in ether (50 ml) was added over a period of 1 h to pentachlorophenyllithium (0.05 mole) in hexane (22.5 ml) prepared in diethyl ether solution[18]. The reaction mixture was kept at −5° during the addition, and then it was allowed to come to its ambient temperature with stirring for 24 h. The solution was filtered and solvent was removed *in vacuo* to give a pale brown solid (22 g) which after sublimation (120°/0.01 mm) and recrystallisation from ethanol gave white needles of (pentachlorophenyl)-trimethyltin, (11.5 g, 56%) m.p. 119–120°.

Attempted preparation of (pentachloroethyl)trimethyltin. Pentachloroethane (1.54 g, 76 mmoles) and (dimethylamino)trimethyltin (1.62 g, 78 mmoles) were mixed at 0° and then allowed to come to room temp. for 15 min. Volatile products were removed by vacuum transfer to give $Me_3SnCl\cdot HNMe_2$ (1.08 g, 44 mmoles) identified by comparison of its IR spectrum with that of an authentic sample, and by its ^{1}H NMR spectrum which showed bands at τ 9.3 (Sn-Me, $I=31$), τ 7.5 (N-Me, $I=18$), and τ 5.7 (N-H, $I=4$). I (integrated area ratio) should be 27 : 18 : 3.

Dimethyl(trichloromethyl)tin chloride. Excess of boron trichloride was condensed into a Carius tube containing (trichloromethyl)trimethyltin (2.38 g, 84 mmoles). The tube was sealed off *in vacuo* and left at 25° for 16 h. Volatile products were removed by vacuum transfer to give a white solid which was sublimed (40°/0.5 mm) to yield white crystals of dimethyl(trichloromethyl)tin chloride, (1.88 g, 62 mmoles, 74%) m.p. 74–76°. (Found: C, 11.89; H, 1.98. $C_3H_6Cl_4Sn$ calcd.: C, 11.91; H, 2.00%.)

The m.p. of samples obtained from other preparations was sometimes higher than 74–76°, but inferior analytical data were obtained for such samples. The IR spectrum (Nujol) showed bands at 1200 w, 780 m, 725 s, and 705 s cm^{-1}. The ^{1}H NMR spectrum showed a singlet at τ 8.98 (Sn-Me). $J(^{119}\text{Sn–H})$ 63.4, $J(^{117}\text{Sn–H})$ 60.4 c/sec.

Reactions of dimethyl(trichloromethyl)tin chloride

(*a*) *Thermal decomposition.* Dimethyl(trichloromethyl)tin chloride (0.45 g, 14.7 mmoles) was heated at 72° in an evacuated ampoule for 16 h. After this time, dimethyl(trichloromethyl)tin chloride (0.33 g, 73%) was recovered by sublimation. This sample was heated at 120° for a further 20 h. The volatile product was collected by vacuum transfer and identified as tetrachloroethylene (0.026 g, 35%). The white solid residue was sublimed (40°/0.5 mm) to give dimethyltin dichloride (0.132 g, 55%) identified by its m.p. 105–106° (lit.[39]: 106°) and IR spectrum.

(*b*) *Hydrolysis.* Dimethyl(trichloromethyl)tin chloride (1.20 g, 39.6 mmoles) and water (1 ml) were heated at 60° for 6 h in a sealed ampoule. The volatile products were shown to contain chloroform by IR spectroscopy. Sublimation of the solid products gave dimethyltin dichloride (0.207 g, 9.4 mmoles) m.p. 104–106°. An involatile white powder (0.293 g) m.p. >300° was also obtained and it was shown to be 1,1,3,3,-tetramethyl-1,3-dichlorodistannoxane. (Found: C, 12.31; H, 2.95; Cl, 18.37; Sn, 60.46. $C_4H_{12}Cl_2Sn_2O$ calcd.: C, 12.49; H, 3.15; Cl, 18.44; Sn, 61.73%.)

(*c*) *With boron trichloride.* Excess of boron trichloride and dimethyl(trichloromethyl)tin chloride (1.25 g, 41.2 mmoles) were heated in a sealed Carius tube at 60°

for 20 h. Volatile products were removed by vacuum transfer to give a white solid residue which, on sublimation (40°/0.05 mm) gave dimethyltin dichloride, (0.491 g, 22.3 mmoles, 54%) m.p. 105–106°.

Hydrolysis of (pentachlorophenyl)trimethyltin

(*a*) *With alcoholic alkali.* (Pentachlorophenyl)trimethyltin (0.60 g, 15 mmoles) and sodium hydroxide (0.5 g) in aqueous ethanol/acetone (20 ml/20 ml) was left at 23° for 12 h. Removal of solvent gave pentachlorobenzene (0.32 g, 88%) identified by its IR spectrum and m.p. 84–86° (lit.[40]: m.p. 85–86°).

(*b*) *With aqueous/alcoholic potassium fluoride.* (Pentachlorophenyl)trimethyltin (0.4 g) was refluxed for 10 min in aqueous ethanol (5 ml/10 ml). When the solution was cooled, white crystals were deposited which were shown to be unchanged (pentachlorophenyl)trimethyltin (IR and m.p.).

(Pentachlorophenyl)trimethyltin (0.40 g, 10 mmoles) in aqueous ethanol (5 ml/10 ml) containing a few crystals of potassium fluoride was refluxed for 10 min. When the solution was cooled, addition of water gave a white precipitate of pentachlorobenzene (0.20 g, 83%) identified by its m.p. 83–85° and IR spectrum.

(Pentachlorophenyl)boron dichloride

(Pentachlorophenyl)trimethyltin (2.30 g, 56 mmoles) and boron trichloride (1.35 g, 115 mmoles) in a sealed, evacuated Carius tube did not react at 25°, so the tube was heated at 110° for 15 h. The tube was cooled and volatile products were collected by vacuum transfer and shown to be methylboron dichloride (0.52 g, 54 mmoles). (Found: mol. wt., 95.5. CH_3BCl_2 calcd.: mol. wt., 96.7.)

The white solid residue in the Carius tube was transferred, under nitrogen, to a sublimation apparatus. Sublimation (25°/0.01 mm) gave dimethyltin dichloride (1.14 g, 52 mmoles) identified by its m.p. 103–105° and IR spectrum. Further sublimation (100°/0.01 mm) gave white crystals of (pentachlorophenyl)boron dichloride (1.65 g, 50 mmoles 90%) m.p. 119–121° (sealed tube), which was characterised by the preparation of two derivatives (see below).

Bis(dimethylamino)(pentachlorophenyl)borane

(Pentachlorophenyl)boron dichloride (1.65 g, 50 mmoles) in benzene (40 ml) was treated with excess of dimethylamine. Dimethylamine hydrochloride (0.383 g, 47 mmoles) was filtered off and solvent was removed *in vacuo* to give a white solid residue. Sublimation (25°/0.01 mm) gave pentachlorobenzene (0.1 g) and (60°/0.01 mm) bis(dimethylamino)(pentachlorophenyl)borane (1.36 g, 39 mmoles) m.p. 96–99°. (Found: C, 33.93; H, 3.41; N, 7.45. $C_{10}H_{12}BCl_5N_2$ calcd.: C, 34.47; H, 3.47; N, 8.04%.)

Pentachlorophenylboronic acid

5 ml of *N* HCl was added to (pentachlorophenyl)boron dichloride (1.21 g, 37 mmoles) in acetone (30 ml) at −78°. The solution was allowed to come to room temperature and solvent was removed *in vacuo* to give white crystals (1.03 g) of pentachlorophenylboronic acid which had m.p. >360° after recrystallisation from benzene. The IR spectrum (Nujol) showed a broad band at 3300 m cm^{-1}. (Found: C, 24.44; H, 1.31; Cl, 59.73. $C_6H_2BCl_5O_2$ calcd.: C, 24.50; H, 0.69; Cl, 60.28%.)

Thermal decomposition of (pentachlorophenyl) trimethyltin

(Pentachlorophenyl)trimethyltin (3.75 g, 91 mmoles) was heated at 300° for 4 h in a sealed, evacuated tube. The tube was cooled and the contents of the tube were extracted with ether (3×30 ml) and insoluble brown solid (0.82 g) was filtered off. Dry ammonia gas was bubbled into the ethereal soln. for 30 min, and the white precipitate of $Me_3SnCl \cdot NH_3$ (1.70 g) was collected by filtration and identified by comparison of its IR spectrum with that of an authentic sample. This corresponds to an 87% yield of trimethyltin chloride. Ether was removed from the filtrate *in vacuo* to give a pale brown solid (1.45 g). Sublimation (80°/0.05 mm) gave pentachlorobenzene (0.06 g) and at (200°/0.01 mm) white crystals (0.1 g) with m.p. 165–175° whose IR spectrum showed a strong band at 1340 cm^{-1}. The ^1H NMR spectrum indicated the absence of protons in this sample. (Found: C, 32.72; H, 0.19; Cl, 67.08. $(C_6Cl_4)_n$ calcd.: C, 33.70; H, 0.0; Cl, 66.30%.)

The mass spectrum of this sample indicates that it is a mixture of perchloropolyphenylenes.

ACKNOWLEDGEMENTS

One of us (B.D.) wishes to thank the S.R.C. for an Advanced Course Studentship. The authors thank Professor C. Eaborn and Dr. D. R. M. Walton for their interest, Mr. R. Suffolk for NMR spectra.

REFERENCES

1 J. Villieras, *Compt. Rend.*, 261 (1965) 4137.
2 W. T. Miller and D. M. Whalen, *J. Amer. Chem. Soc.*, 86 (1964) 2089.
3 D. F. Hoeg, D. I. Lusk and A. L. Crumbliss, *J. Amer. Chem. Soc.*, 87 (1965) 4147.
4 G. Köbrich, K. Flory and W. Drischel, *Angew. Chem.*, 76 (1964) 536.
5 W. R. Bamford and B. C. Pant, *J. Chem. Soc., C*, (1967) 1470.
6 D. Seyferth, F. M. Armbrecht, B. Prokai and R. J. Cross, *J. Organometal. Chem.*, 6 (1966) 573.
7 D. Seyferth, J. Y-P. Mui and J. M. Burlitch, *J. Amer. Chem. Soc.*, 89 (1967) 4953 and references cited therein.
8 G. D. Cooper and A. R. Gilbert, *J. Amer. Chem. Soc.*, 82 (1960) 5042.
9 H. Gilman and L. S. Miller, *J. Amer. Chem. Soc.*, 73 (1951) 968.
10 T. Logan, *J. Org. Chem.*, 28 (1963) 1129.
11 A. G. Davies and T. N. Mitchell, *J. Organometal. Chem.*, 6 (1966) 569.
12 A. G. Davies and W. R. Symes, *J. Organometal. Chem.*, 5 (1966) 394.
13 A. G. Davies and R. J. Puddephatt, *J. Organometal. Chem.*, 5 (1966) 592.
14 L. C. Willemsens and G. J. M. Van der Kerk, *Investigations in the field of organolead chemistry*, International Lead and Zinc Organisation, New York, 1965, pp. 42, 98.
15 J. F. Nixon, *J. Inorg. Nucl. Chem.*, 27 (1965) 1281.
16 S. D. Rosenberg, J. J. Walburn and H. E. Ramsden, *J. Org. Chem.*, 22 (1957) 1606.
17 C. Tamborski, E. J. Soloski and C. E. Dills, *Chem. Ind. (London)*, (1965) 2067.
18 M. D. Rausch, F. E. Tibbetts and H. B. Gordon, *J. Organometal. Chem.*, 5 (1966) 493.
19 F. E. Paulik, S. I. E. Green and R. E. Dessy, *J. Organometal. Chem.*, 3 (1965) 229.
20 G. B. Deacon and P. W. Felder, *Aust. J. Chem.*, (1966) 2381.
21 P. J. Morris, F. W. G. Fearon and H. Gilman, *J. Organometal. Chem.*, 9 (1967) 427 and references cited therein.
22 H. Gilman and S.-Y. Sim, *J. Organometal. Chem.*, 7 (1967) 249.
23 J. Chatt and B. L. Shaw, *J. Chem. Soc.*, (1961) 285.
24 D. J. Cardin and M. F. Lappert, *Chem. Commun.*, (1967) 1034.
25 R. D. Chambers, H. C. Clark and C. J. Willis, *Can. J. Chem.*, 39 (1961) 131.

26 H. D. Kaesz, S. L. Stafford and F. G. A. Stone, *J. Amer. Chem. Soc.*, 81 (1959) 6336.
27 R. D. Chambers and T. Chivers, *J. Chem. Soc.*, (1964) 4782.
28 R. D. Chambers and T. Chivers, *J. Chem. Soc.*, (1965) 3933.
29 D. Seyferth and A. B. Evnin, *J. Amer. Chem. Soc.*, 89 (1967) 1468.
30 H. Heaney and J. M. Jablonski, *Tetrahedron Lett.*, (1966) 4529.
31 M. Ballester and J. Castaner, *J. Amer. Chem. Soc.*, 82 (1960) 4259.
32 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, New York, 1960, p. 224.
33 Ref. 32. p. 260.
34 H. A. Skinner and L. E. Sutton. *Trans. Faraday Soc.*, 40 (1944) 164.
35 R. C. Poller, *J. Organometal. Chem.*, 3 (1965) 321.
36 M. V. Kashutina and O. Yu. Okhlobystin, *J. Organometal. Chem.*, 9 (1967) 5.
37 K. Jones and M. F. Lappert, *J. Chem. Soc.*, (1965) 1944.
38 D. Seyferth and R. H. Towe, *Inorg. Chem.*, 2 (1962) 185.
39 G. E. Coates, *Organometallic Compounds*, Methuen, London, 1960, p. 186.
40 A. Ladenberg, *Anal. Chem.*, 172 (1874) 344.
41 D. Seyferth, R. J. Cross and B. Prokai, *J. Organometal. Chem.*, 7 (1967) P20.
42 T. Chivers and B. David, *J. Organometal. Chem.*, 10 (1967) P35.