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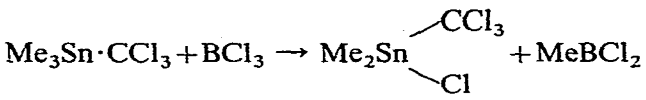
PRELIMINARY NOTE

Chlorocarbon derivatives of tin

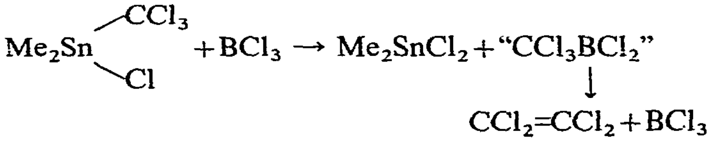
Current interest[1–5] in chlorocarbon derivatives of tin prompts this preliminary report of our work in this field. The preparation of trichloromethyltrimethyltin by two different routes has been described[1,3]. One group of workers reports that in reactions with bromine[1] and hydrogen chloride[2], trichloromethyltrialkyltins release a trichloromethyl group.

We have found that boron trichloride cleaves a methyl group from trichloromethyltrimethyltin at 25° to give trichloromethyldimethyltin chloride as a white crystalline solid m.p. 74–76° in 74 % yield, readily purified by sublimation (40°/0.5 mm).



$$Me_3Sn{\cdot}CCl_3 + BCl_3 \rightarrow Me_2Sn\begin{smallmatrix}\diagup CCl_3\\ \diagdown Cl\end{smallmatrix} + MeBCl_2$$

The proton magnetic resonance spectrum of trichloromethyldimethyltin chloride shows a singlet, τ 8.98 (CH_3Sn), $J(^{119}Sn{-}CH_3)$ 63.4, $J(^{117}Sn{-}CH_3)$ 60.4 cps. The infrared spectrum (Nujol) has bands at 1200(w), 780(m), 725(s) and 705(s) cm^{-1}. Trichloromethyldimethyltin chloride shows a marked enhancement of stability towards atmospheric hydrolysis when compared to trichloromethyltrimethyltin. Whereas trichloromethyltrimethyltin is rapidly converted to trimethyltin hydroxide and chloroform on exposure to moist air, trichloromethyldimethyltin chloride is unchanged after several weeks in a sample bottle. Trichloromethyldimethyltin chloride decomposes when heated above its melting point. For example, after 16 h at 72° trichloromethyldimethyltin chloride was recovered in 85 % yield, but at 120° considerable decomposition occurred to give dimethyltin dichloride. With boron trichloride at 60° a trichloromethyl group is cleaved from trichloromethyldimethyltin chloride to give dimethyltin dichloride.



$$\begin{array}{l} Me_2Sn\begin{smallmatrix}\diagup CCl_3\\ \diagdown Cl\end{smallmatrix} + BCl_3 \rightarrow Me_2SnCl_2 + \text{“}CCl_3BCl_2\text{”} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad CCl_2{=}CCl_2 + BCl_3 \end{array}$$

Davies and Mitchell[1] prepared trichloromethyltrimethyltin by treating diethylaminotrimethyltin with an excess of chloroform. We have confirmed this result, and obtained yields of 72 % using dimethylaminotrimethyltin and performing the addition at 0°. We have explored the possibility of extending this reaction to the preparation of other perhalogenated derivatives of tin. Trichloroethylene and dimethylaminotrimethyltin, after 15 min reflux, give trichlorovinyltrimethyltin (b.p. 111°/20 mm) in 80 % yield, whose IR spectrum shows bands at 3000 (m), 2930 (m), 1540 (s), 1200 (w), 934 (s), 835 (s), 786 (s), 735 (m) and 697 (m) cm^{-1}. A strong band at 1545 cm^{-1} (C=C stretch) has been reported for trichlorovinylmercurials[6].

2-*H*-Heptafluoropropane (p*K*a ~ 20)[7] gives a quantitative yield of trimethyltin fluoride when reacted with dimethylaminotrimethyltin at 25° in a sealed tube[8]. Pentachlorobenzene did not react with dimethylaminotrimethyltin even in refluxing hexane.

Pentachlorophenyltrimethyltin (m.p. 119–120°) can however be obtained in 50% yields by treatment of trimethyltin chloride with pentachlorophenyllithium in diethyl ether or pentachlorophenylmagnesium chloride in THF. Reaction with boron trichloride at 100° in a sealed tube cleaves a pentachlorophenyl group from tin to give pentachlorophenylboron dichloride, a white solid (m.p. 119–121°), which fumes slightly in moist air.

$$Me_3SnC_6Cl_5 + 2\,BCl_3 \xrightarrow{100^\circ} Me_2SnCl_2 + C_6Cl_5BCl_2 + MeBCl_2$$

Pentachlorophenylboron dichloride is readily purified by sublimation ($100^\circ/10^{-2}$ mm) after removal of dimethyltin dichloride ($25^\circ/10^{-2}$ mm).

Further work with chlorocarbon tin compounds is in progress with a view to establishing the nature and extent of tin–chlorine interactions in these derivatives. All new compounds reported herein had satisfactory analytical data.

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1 A. G. Davies and T. N. Mitchell, *J. Organometal. Chem.*, 6 (1966) 568.
2 A. G. Davies and W. R. Symes, *J. Organometal. Chem.*, 5 (1966) 394.
3 D. Seyferth, F. M. Armbrecht, B. Prokai and R. J. Cross, *J. Organometal. Chem.*, 6 (1966) 573.
4 H. Gilman and S-Y. Sim, *J. Organometal. Chem.*, 7 (1967) 249.
5 D. Seyferth and A. B. Evnin, *J. Am. Chem. Soc.*, 89 (1967) 1468.
6 D. Seyferth and R. H. Towe, *Inorg. Chem.*, 1 (1962) 185.
7 S. Andreades, *J. Am. Chem. Soc.*, 86 (1964) 2003.
8 T. Chivers, unpublished observation.

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