

THE CLEAVAGE OF ORGANOTIN-SULPHUR COMPOUNDS BY HALIDES

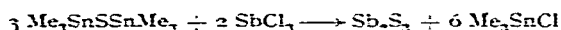
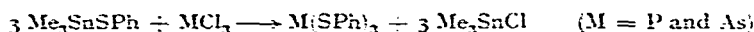
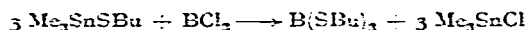
E. W. ABEL, D. B. BRADY AND B. C. CROSSE

Department of Inorganic Chemistry, The University, Bristol 8 (England)

(Received July 30th, 1965)

Recent studies of organotin compounds containing one or more tin-sulphur bonds have shown them to be more strongly basic than simple organic sulphides¹. This, coupled with their stability, *e.g.* in aqueous conditions², suggested that they might have an interest as sulphur donor ligands. Further, it appeared that two alkylthio groups on the large tin(IV) atom, were ideally placed to give rise to a bidentate ligand.

Efforts to prepare a co-ordination complex of (*n*-butylthio)trimethyltin and boron trichloride, analogous to those formed between boron trichloride and the dialkyl sulphides³⁻⁵ resulted in the isolation of trimethyltin chloride and (alkylthio)boron derivatives. Any co-ordination complex, if formed, underwent immediate fission of the tin-sulphur bond to form tin-chlorine and boron-sulphur bonds. Thus the (alkylthio)-tin compounds appeared to behave no differently from the analogous organosilicon compounds⁶. In order to check the generality of this halide fission, the tin-sulphur compounds were also made to undergo reaction with phosphorus², arsenic and antimony halides. In each case fission was complete.



We note that bis(triethyltin) sulphide has been reported to react with phosphorus, arsenic and stannic chlorides to produce the corresponding sulphides⁷. The reactions of tin-sulphur compounds with non-metal halides thus appear to parallel those of the already widely investigated^{6,8-12} thiosilanes so closely as to merit little further investigation.

In addition to the above reactions, mono- and bifunctional (alkylthio)tins were treated with halides of mercury, cadmium and platinum in an effort to obtain co-ordinated derivatives. In all cases, however, cleavage of the tin-sulphur bonds took place with the results summarized in Table I. Fission by mercuric chloride of those (alkylthio)tin compounds investigated by us invariably led to the formation of the mercury dimercaptide $\text{Hg}(\text{SR})_2$, whereas the corresponding reaction with the tetrakis-(alkylthio)tins is reported¹⁵ to give only the partially thiolated products, RSHgCl . We did, however, obtain the half mercaptides RSHgX from the fission of (alkylthio)tins

TABLE I

REACTION OF ORGANOTIN-SULPHUR COMPOUNDS WITH METAL HALIDES

Reagents	Mol. ratio	Product	Yield (%)	Found (%)		Calc. (%)	
				C	H	C	H
HgCl ₂ + Me ₃ SnSMe	1:2	Hg(SMe) ₂ ^a	93	8.2	2.2	8.2	2.1
HgCl ₂ + Me ₂ Sn(SMe) ₂	1:1	Hg(SMe) ₂ ^b	91	8.1	2.4	8.2	2.1
HgCl ₂ + Et ₂ Sn(SMe) ₂	1:1	Hg(SMe) ₂ ^c	85	8.0	2.2	8.2	2.1
HgCl ₂ + Me ₃ SnSEt	1:2	Hg(SEt) ₂ ^d	82	15.0	3.3	14.9	3.1
HgBr ₂ + Me ₂ Sn(SMe) ₂	1:1	BrHgSMe	94	3.8	0.8	3.7	0.9
HgI ₂ + Me ₂ Sn(SMe) ₂	1:1	IHgSMe	66	3.2	1.0	3.2	0.8
CdCl ₂ + Me ₂ Sn(SMe) ₂	1:1	ClCdSMe ^e	95	5.9	1.5	6.2	1.6
CdBr ₂ + Me ₂ Sn(SMe) ₂	1:1	BrCdSMe	94	4.9	1.1	5.0	1.3
HgCl ₂ + Me ₂ Sn(SCH ₂) ₂	1:1	(HgSC ₂ H ₄ S) _n	92	8.2	1.4	8.2	1.4
HgCl ₂ + (Me ₃ Sn) ₂ S	1:1	HgS ^f	95				
K ₂ PtCl ₄ + Et ₂ Sn(SMe) ₂	1:1	Pt(SMe) ₂ ~	100	8.0	2.0	8.3	2.1
K ₂ PtCl ₄ + Me ₃ SnSBu	1:2	Pt(SBu) ₂	91	26.0	4.9	25.7	4.9
K ₂ PtCl ₄ + Me ₂ Sn(SET) ₂	1:1	Pt(SET) ₂ ~	100	15.8	3.3	15.1	3.2

^a M.p. 176–177°, lit.¹³ 176°. ^b M.p. 175–176°, lit.¹³ 176°. ^c M.p. 174–176°, lit.¹³ 176°. ^d M.p. 76°, lit.¹⁴ 74–75°. ^e Cl found 18.3%, calcd. 18.2%. ^f This reaction involves an orange-yellow intermediate, possibly Me₃SnSHgCl, which could not be isolated.

by mercuric bromide and iodide. Whereas the compound CH₂SSn(CH₃)₂SCH₂ is able to exist as a ring, the product of its fission by mercuric chloride is a polymer, (CH₂S-HgSCH₂)_n, due to the linear nature of the HgII bonds.

(Alkylthio)tin compounds also react with the halides of palladium, zinc, indium and other metals, but the products are either unstable, inseparable mixtures, or could not be isolated analytically pure. The reactions of nickel chloride have, however, proved to be particularly interesting, and will be the subject of a separate communication.

EXPERIMENTAL

Interaction of (*n*-butylthio)trimethyltin and boron trichloride

(*n*-Butylthio)trimethyltin (24.9 g, 0.10 mole) in pentane (20 ml) was added slowly to boron trichloride (3.9 g, 0.03 mole) in pentane (10 ml) at –80°. The mixture was allowed to warm to room temperature, and the pentane was removed by distillation. Large crystals of trimethyltin chloride (8.7 g, 44%), m.p. 37–38°, separated out and were removed. Fractional distillation of the remaining oil gave initially a further quantity of trimethyltin chloride followed by tri-*n*-butyl thioborate (5.0 g, 54%) b.p. 130°/0.4 mm, *n*_D²⁰ 1.5230 (lit.⁶ *n*_D²⁰ 1.5227).

Interaction of (phenylthio)trimethyltin and arsenic trichloride

Arsenic trichloride (1.45 g, 0.008 mole) was added to (phenylthio)trimethyltin (7.0 g, 0.026 mole) at 0°. After warming, the mixture was filtered. The residual solid was recrystallized from benzene to give triphenyl thioarsenite (1.1 g, 34%), m.p. 90° (lit.¹⁶ 95°) (Found: C, 51.1; H, 3.5. C₁₈H₁₅AsS₃ calcd.: C, 53.7; H, 3.8%). Distillation of the filtrate gave trimethyltin chloride (4.8 g, 92%), b.p. 150–152°, m.p. 37–38°.

Interaction of bis(trimethyltin) sulphide and antimony trichloride

Bis(trimethyltin) sulphide (3.6 g, 0.0099 mole) was added to antimony trichloride (1.5 g, 0.0066 mole) in dry benzene (10 ml). The orange precipitate formed was washed with benzene and vacuum dried to give antimony sulphide (1.0 g, 90 %). Benzene was distilled from the residual solution to leave crystals of trimethyltin chloride, m.p. 35–37°.

Reactions of organotin-sulphur compounds with metal halides

These reactions were all carried out by the direct interaction (on ca. 0.5 g scale) in ethanolic solution, or in the case of platinum, aqueous ethanolic solution. These reactions are summarized in Table 1. The mercury mercaptides, $\text{Hg}(\text{SR})_2$, were recrystallized from ethanol; the other mercaptides, being quite insoluble in organic solvents, were washed with ethanol and light petroleum, and vacuum dried.

ACKNOWLEDGEMENTS

We are grateful to the International Tin Research Council and the Scientific Research Council for grants in aid of this work.

SUMMARY

The interaction of organometallic compounds containing tin-sulphur bonds with non-metal and metal halides has been shown to result invariably in the fission of the tin-sulphur bonds.

REFERENCES

- 1 E. W. ABEL, D. A. ARMITAGE AND D. B. BRADY, *Trans. Faraday Soc.*, to be published.
- 2 E. W. ABEL AND D. B. BRADY, *J. Chem. Soc.*, (1965) 1192.
- 3 G. M. PHILLIPS, J. S. HUNTER AND L. E. SUTTON, *J. Chem. Soc.*, (1945) 146.
- 4 M. F. LAPPERT, *J. Chem. Soc.*, (1953) 2784.
- 5 N. I. KULEVSKY, *Dissertation Abstr.*, 24 (1963) 536.
- 6 E. W. ABEL, D. A. ARMITAGE AND R. P. BUSH, *J. Chem. Soc.*, (1965) 3045.
- 7 H. H. ANDERSON, *J. Org. Chem.*, 19 (1954) 1766.
- 8 E. W. ABEL, *J. Chem. Soc.*, (1961) 4933.
- 9 E. W. ABEL, D. A. ARMITAGE AND R. P. BUSH, *J. Chem. Soc.*, (1964) 2455.
- 10 E. W. ABEL, D. A. ARMITAGE AND R. P. BUSH, *J. Chem. Soc.*, (1964) 5584.
- 11 E. W. ABEL AND D. A. ARMITAGE, *J. Chem. Soc.*, (1964) 5975.
- 12 E. W. ABEL, D. A. ARMITAGE AND D. B. BRADY, *J. Organometal. Chem.*, 5 (1966) 130.
- 13 S. BLACKBURN AND F. CHALLENGER, *J. Chem. Soc.*, (1938) 1872.
- 14 T. KONDO, *Yakugaku Zasshi*, 84 (1964) 137; *Chem. Abstr.*, 61 (1964) 3136.
- 15 H. J. BACKER AND J. KRAMER, *Rec. Trav. Chim.*, 53 (1934) 1101.
- 16 R. KLEMENT AND R. REUBER, *Ber.*, 68 (1935) 1761.