SOME SYNTHESES AND REACTIONS OF GROUP IVB ORGANOMETALLIC COMPOUNDS CONTAINING NITROGEN, OXYGEN, SULPHUR AND SELENIUM

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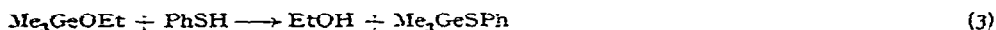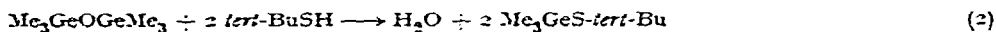
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The requirement of a wide variety of amines, ethers, sulphides and selenides of the Group IVB elements for base strength measurements[1] and fission reactions[2] has caused us to explore a range of metathetical reactions for the preparation of these compounds. A number of these have proved to be very satisfactory methods, and also to involve many reaction types not previously reported.

The reaction of organosilicon sulphur derivatives with a variety of covalent halides has been reported to cause fission of the silicon sulphur bond[3,4]. We now find a similar reaction occurs between (alkylthio)trimethylsilanes and, respectively, trimethylgermanium and trimethyltin halides.

$$Me_3SiSR + Me_3MX \longrightarrow Me_3MSR + Me_3SiX \qquad (M = Ge, Sn; X = Cl, Br) \qquad (1)$$
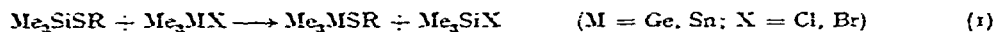
These reactions proceed smoothly under conditions of reflux, and the halogeno-silane produced may be removed by continuous distillation to leave only the liquid product. The method thus avoids the formation of sometimes troublesome solid by-products.

Although it is not possible to prepare organosulphur derivatives of silicon from corresponding organo-oxygen derivatives, the direct reaction of thiols with organotin oxygen compounds is widely used as a preparative method for alkyl- and arylthio-derivatives of tin[5]. Among other reasons, such a change in the reactivity may be due to the possible reversed order of metal–oxygen and metal–sulphur bond strengths in going from silicon to tin[6]. The corresponding reactions for germanium are therefore of particular interest. It has been reported that hexaethyldigermoxane reacted with thiophenol to produce water and (phenylthio)triethylgermane, and further, that a similar reaction involving ethanethiol gave very little of the thiogermane[7]. We have now carried out the reaction between hexamethyldigermoxane and *tert*-butanethiol, and obtained (*tert*-butylthio)trimethylgermane (eqn. 2).

$$Me_3GeOGeMe_3 + 2 \; tert\text{-BuSH} \longrightarrow H_2O + 2 \; Me_3GeS\text{-}tert\text{-Bu} \qquad (2)$$

$$Me_3GeOEt + PhSH \longrightarrow EtOH + Me_3GeSPh \qquad (3)$$

A similar type of reaction between ethoxytrimethylgermane and thiophenol was exothermic at room temperature and gave ethyl alcohol and the (phenylthio)tri-methylgermane (eqn. 3). These experiments would appear to indicate the favoured formation of the germanium–sulphur over germanium–oxygen bonds, under these conditions.

The interconversion of silicon–nitrogen and silicon–sulphur bonds appears to be reversible[8], and depends upon the ease of removal (normally by distillation) of one of the products. In the case of the action of thiols upon (diethylamino)trimethylgermane and (diethylamino)trimethyltin, the considerable exothermicity of the reactions (eqn. 4) makes it unlikely that the reactions would be reversible.
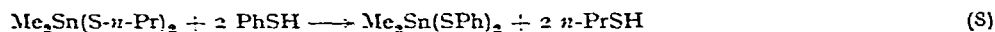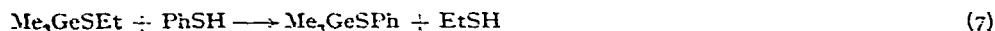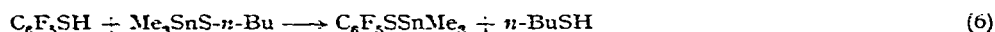
$$Me_3MNEt_2 + RSH \longrightarrow Me_3MSR + Et_2NH \qquad (M = Ge, Sn) \tag{4}$$
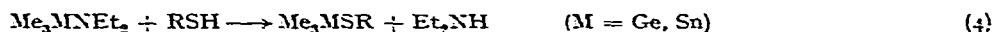
The displacement of dialkylamino groups from tin by a wide range of hydrogen containing compounds has been recently reported[9].

The interaction of thiols with organotin halides yields the (alkylthio)tin compounds in aqueous conditions[10]. This method has now been extended to selenium compounds, and we find that benzeneselenol and trimethyltin chloride react in water in the presence of base to give a good yield of (phenylseleno)trimethyltin (eqn. 5).
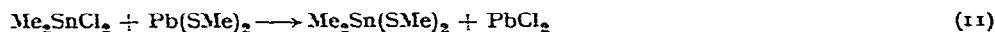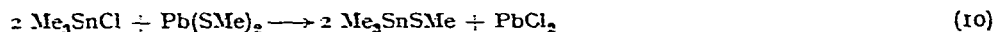
$$PhSeH + Me_3SnCl \xrightarrow{OH^- Aq.} Me_3SnSePh \tag{5}$$

A number of other replacement reactions best summarised in equations (6)–(8) have also been used as preparative methods.

$$C_6F_5SH + Me_3SnS\text{-}n\text{-}Bu \longrightarrow C_6F_5SSnMe_3 + n\text{-}BuSH \tag{6}$$

$$Me_3GeSEt + PhSH \longrightarrow Me_3GeSPh + EtSH \tag{7}$$

$$Me_2Sn(S\text{-}n\text{-}Pr)_2 + 2\ PhSH \longrightarrow Me_2Sn(SPh)_2 + 2\ n\text{-}PrSH \tag{8}$$

Lead methylmercaptide has been found to have somewhat lower solubility than the other lead mercaptides, and this may account for the surprising report[11] that lead methylmercaptide does not react with trimethylchlorosilane to produce (methylthio)trimethylsilane, in sharp contrast to the extensive preparation of other (alkylthio)trimethylsilanes by this method[12]. We find, however, that trimethylchlorosilane does in fact react with lead methylmercaptide to produce a very good yield of (methylthio)trimethylsilane (eqn. 9), the only requirement being that diethyl ether be present to improve solubility.

$$Pb(SMe)_2 + 2\ Me_3SiCl \longrightarrow 2\ Me_3SiSMe + PbCl_2 \tag{9}$$
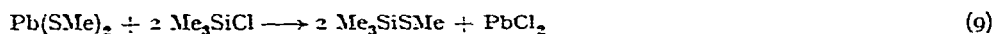
Further use of lead methylmercaptide has been made for the synthesis of (methylthio)trimethyltin and bis(methylthio)dimethyltin (eqns. 10 and 11).

$$2\ Me_3SnCl + Pb(SMe)_2 \longrightarrow 2\ Me_3SnSMe + PbCl_2 \tag{10}$$

$$Me_2SnCl_2 + Pb(SMe)_2 \longrightarrow Me_2Sn(SMe)_2 + PbCl_2 \tag{11}$$

The new compound tris(methylthio)methyltin has been qrepared by the reaction of methyltin tribromide with methanethiol in apueous solution.

EXPERIMENTAL

Preparations and techniques

A number of the reactants required for this work, are themselves new compounds, and their preparation is reported below. Further, some improved methods for the preparation of other reagents are also reported.

Trimethylbromogermane. Tetramethylgermane was prepared in 90 % yield by the method of Brown and Fowles[13], and to 84.5 g of this was added aluminium chloride (0.5 g). Bromine (102 g, 1 mol.) was slowly added, and was accompanied by a vigorous reaction. After stirring for 2 h distillation gave trimethylbromogermane (104 g, 83 %). This was shaken with a little mercury to remove dissolved iodine, and subsequent distillation gave pure trimethylbromogermane, b.p. 113°, n_D^{25} 1.4658, d_4^{20} 1.55 (lit.[14] b.p. 115°, n_D^{20} 1.4660, d_4^{20} 1.5486). (Found: C, 18.2; H, 4.6. C_3H_9BrGe calcd.: C, 18.2; H, 4.6 %.)

(Diethylamino)trimethylgermane. Bromobenzene (15.7 g, 1 mol.) was added to lithium (1.8 g, 1.25 mol.) in diethyl ether (300 ml); after the initial reaction had subsided, the mixture was heated under reflux for one hour. After cooling, diethylamine (7.3 g, 1 mol.) was added and the mixture heated for a further one hour. Trimethylbromogermane was then added, and the whole heated under reflux for 24 h. Filtration and subsequent distillation of the filtrate gave (diethylamino)trimethylgermane (9.75 g, 51 %), b.p. 138–9°, n_D^{20} 1.4304, d_4^{20} 1.01. (Found: C, 43.1; H, 9.5. $C_7H_{19}GeN$ calcd.: C, 44.4; H, 10.0 %.)

Hexamethyldigermoxane. Trimethylbromogermane (20 g) was added to an excess of aqueous alkali with constant shaking. Diethyl ether (25 ml) was then used to extract the product. After drying with anhydrous sodium sulphate the ether extract was distilled to yield hexamethyldigermoxane[15] (7.2 g, 57 %), b.p. 137°, n_D^{21} 1.4290. d_4^{20} 1.22. (Found: C, 28.7; H, 7.3. $C_6H_{18}OGe_2$ calcd.: C, 28.7; H, 7.2 %.)

Ethoxytrimethylgermane. Trimethylbromogermane (16.0 g) in diethyl ether (25 ml) was slowly added to an excess of sodium ethoxide, and the resulting mixture was heated under reflux for 12 h. All volatile material was then removed at reduced pressure (0.01 mm) and allowed to stand over sodium (5 h). Volatile materials were then removed at reduced pressure (0.01 mm) and fractionally distilled to give ethoxytrimethylgermane (8.0 g, 61 %), b.p. 100–101°, n_D^{20} 1.4067, d_4^{20} 1.06. (Found: C, 36.8; H, 8.9. $C_5H_{14}GeO$ calcd.: C, 36.9; H, 8.7 %.)

(Ethylthio)trimethylgermane. Trimethylbromogermane (19.8 g) was added to an excess of sodium ethylmercaptide in diethyl ether, and the mixture heated under reflux for 12 h. Subsequently, all volatile materials were removed at reduced pressure (0.01 mm) and fractionally distilled to give (ethylthio)trimethylgermane (16.7 g, 94 %). b.p. 148°, n_D^{20} 1.4788, d_4^{20} 1.10. (Found: C, 34.2; H, 8.0. $C_5H_{14}GeS$ calcd.: C, 33.6; H, 7.9 %.)

Interactions

Trimethylbromogermane and (ethylthio)trimethylsilane. The two reactants were heated together under reflux, and over 15 h trimethylbromosilane (5.19 g), b.p. 80°, n_D^{20} 1.4238 was removed. Distillation of the residue yielded (ethylthio)trimethylgermane (4.9 g, 56 %), b.p. 148°, n_D^{20} 1.4779.

Trimethyltin chloride and (isopropylthio)trimethylsilane. The chloride (13.9 g,

1 mol.) was heated with the thiosilane (10.4 g, 1 mol.), and over a period of three days chlorotrimethylsilane (5.3 g, 71 %), b.p. 57.5–59°, n_D^{22} 1.3881, was evolved. The residual liquid was then distilled to produce (isopropylthio)trimethyltin (14.0 g, 84%), b.p. 24–25°/0.01 mm, n_D^{20} 1.5108 (lit.[10] b.p. 182°, n_D^{20} 1.5123). (Found: C, 30.2; H, 6.6. $C_6H_{16}SSn$ calcd.: C, 30.2; H, 6.8 %.)

tert-Butanethiol with hexamethyldigermoxane. The thiol (3.4 g, 1 mol.) and hexamethyldigermoxane (4.7 g, 1 mol.) were mixed at 0°, and then heated for ten minutes. The emulsion produced was dried over anhydrous magnesium sulphate and then filtered. Distillation of the filtrate gave (*tert*-butylthio)trimethylgermane (1.8 g, 23 %), b.p. 25–26°/0.1 mm, n_D^{20} 1.4729, d_4^{20} 1.08. (Found: C, 40.35; H, 8.7. $C_7H_{18}GeS$ calcd.: C, 40.6; H, 8.8 %.)

Ethoxytrimethylgermane and thiophenol. The thiophenol (2.3 g, 1 mol.) was added to ethoxytrimethylgermane (3.4 g, 1 mol.) with the evolution of heat. Subsequent distillation of the product mixture gave ethanol (0.70 g, 73 %), b.p. 78°, n_D^{22} 1.3623, and (phenylthio)trimethylgermane (3.4 g, 72 %), b.p. 37°/0.001 mm, n_D^{23} 1.5560, d_4^{20} 1.20. (Found: C, 47.4; H, 6.1. $C_9H_{14}GeS$ calcd.: C, 47.7; H, 6.2 %.)

n-Butanethiol with (diethylamino)trimethylgermane. Addition of the thiol (2.66 g, 1 mol.) to the aminogermane (5.6 g, 1 mol.) resulted in an exothermic reaction, and subsequent distillation of the resulting mixture gave diethylamine (1.3 g, 60 %- n_D^{22} 1.3844, and (*n*-butylthio)trimethylgermane (5.2 g, 85 %), b.p. 62°/8 mm, n_D^{22} 1.4736, d_4^{20} 1.08. (Found: C, 40.0, H, 8.4. $C_7H_{18}GeS$ calcd.: C, 40.6; H, 8.8 %.)

n-Butanethiol and (diethylamino)trimethyltin. The thiol (7.05 g, 1 mol.) and amino-tin (18.4 g, 1 mol.) reacted exothermically upon mixing and subsequent distillation of the product mixture gave diethylamine (4.4 g, 77 %), b.p. 56°, n_D^{20} 1.3861, and (*n*-butylthio)trimethyltin (18.1 g, 92 %), b.p. 40–42°/0.01 mm, n_D^{20} 1.5090 (lit.[10] b.p. 44°/0.05 mm, n_D^{20} 1.5098). (Found: C, 33.1; H, 7.1. $C_7H_{18}SSn$ calcd.: C, 33.2; H, 7.2 %.)

Benzeneselenol and trimethyltin chloride. The selenol (5.0 g, 1 mol.) was added to the trimethyltin chloride (6.4 g, 1 mol.) in water (30 ml). After slow addition of sodium hydroxide (1.3 g) in water the mixture was stirred for 2 h. The resulting oil was separated from the aqueous layer and washed with water (2 × 50 ml) and then dried over magnesium sulphate. Distillation gave (phenylseleno)trimethyltin (5.0 g, 50 %), b.p. 67–69°/0.001 mm, n_D^{20} 1.6119, d_4^{20} 1.65. (Found: C, 33.7; H, 4.5. $C_9H_{14}SeSn$ calcd.: C, 33.8; H, 4.4 %.) The product is very pale yellow immediately after distillation, but darkens slightly upon storage.

Pentafluorothiophenol and (n-butylthio)trimethyltin. Careful heating of a mixture of pentafluorothiophenol (9.0 g, 1 mol.) and (*n*-butylthio)trimethyltin caused evolution of *n*-butanethiol (2.8 g, 69 %), b.p. 98–99°, n_D^{20} 1.4410. Distillation of the residue gave (pentafluorophenylthio)trimethyltin (12.3 g, 75 %), b.p. 62°/0.001 mm, n_D^{20} 1.5244, d_4^{20} 1.71. (Found: C, 29.9; H, 2.6. $C_9H_9F_5SSn$ calcd.: C, 29.8; H, 2.5 %.)

(Ethylthio)trimethylgermane and thiophenol. Slow fractional distillation of a mixture of thiophenol (4.20 g, 1 mol.) and (ethylthio)trimethylgermane (6.8 g, 1 mol.) gave ethanethiol (1.6 g, 68 %), b.p. 35–36°, n_D^{22} 1.4287, and (phenylthio)trimethylgermane (6.9 g, 80 %), b.p. 37°/0.001 mm, n_D^{20} 1.5564.

Thiophenol and bis(n-propylthio)dimethyltin. After heating the thiophenol (12.6 g, 2 mol) with the bis(*n*-propylthio)dimethyltin (17.0 g, 1 mol.) for 2 h slow distillation gave *n*-propanethiol (6.5 g, 76 %), b.p. 67°, n_D^{20} 1.4378, and subsequently at reduced

pressure bis(phenylthio)dimethyltin (13.6 g, 65 %), b.p. 130–5°/0.001 mm, m.p. 38–39°. (Found: C, 45.6; H, 4.2. $C_{14}H_{18}S_2Sn$ calcd.: C, 45.8; H, 4.2 %.)

Trimethylchlorosilane and lead methylmercaptide. The mercaptide (100 g) was heated under reflux with trimethylchlorosilane (100 ml) and diethyl ether (100 ml) for four days. Subsequent filtration and distillation gave (methylthio)trimethylsilane [59.1 g, 74 % based on Pb(SMe)$_2$], b.p. 110–111°, n_D^{23} 1.4484, d_4^{20} 0.831 (lit.[11] b.p. 110–111°). (Found: C, 39.7; H, 10.1. $C_4H_{12}SSi$ calcd.: C, 39.9; H, 10.1 %.)

Trimethyltin chloride and lead methylmercaptide. Trimethyltin chloride (33.5 g, 2 mol.) in benzene (75 ml) was added to lead methylmercaptide (23.1 g, 1 mol.) in benzene (125 ml), and the mixture heated under reflux for six days. Subsequent filtration and distillation gave (methylthio)trimethyltin (10.2 g, 26 %), b.p. 161–163°, n_D^{20} 1.5285. (Found: C, 22.6; H, 5.7. $C_4H_{12}SSn$ calcd.: C, 22.8; H, 5.7 %.)

Dimethyltin dichloride and lead methylmercaptide. Dimethyltin dichloride (22.0 g, 1 mol.) and lead methylmercaptide (30.0 g, 1 mol.) were heated under reflux in benzene (125 ml) for 24 h. Subsequent filtration and distillation gave bis(methylthio)dimethyltin (17.1 g, 70 %), b.p. 40°/0.03 mm, which was found to be contaminated with halogen, possibly as starting material or half thiolated product. A second careful fractional distillation gave a purer product, b.p. 40°/0.03 mm, n_D^{20} 1.5953. (Found: C, 19.6; H, 4.9. $C_4H_{12}S_2Sn$ calcd.; C, 19.8; H, 5.0 %.)

Methanethiol and methyltin tribromide. Methanethiol was passed under pressure into an aqueous solution of methyltin tribromide (26.1 g, 1 mol.). A solution of sodium hydroxide (8.4 g, 3 mol.) in distilled water (100 ml), was added slowly with vigorous magnetic stirring. A pale yellow oil, and some solid polymer separated. The oil was extracted, washed with water (3 × 50 ml) and dried with magnesium sulphate. Subsequent distillation produced tris(methylthio)methyltin (9.8 g, 51 %), b.p. 75°/0.01 mm, n_D^{23} 1.6352, d_4^{20} 1.63. (Found: C, 17.9; H, 4.6. $C_4H_{12}S_3Sn$ calcd.: C, 17.5; H, 4.4 %.)

ACKNOWLEDGEMENTS

SUMMARY

A number of new metathetical reactions involving group IVB organometallic compounds containing nitrogen, oxygen, sulphur and selenium are recorded. The work has included the preparation of the following new compounds: (diethylamino)trimethylgermane, ethoxytrimethylgermane, (ethylthio)trimethylgermane, (tert-butylthio)trimethylgermane, (phenylthio)trimethylgermane, (n-butylthio)trimethylgermane, (phenylseleno)trimethyltin, (pentafluorophenylthio)trimethyltin, bis(phenylthio)dimethyltin and tris(methylthio)methyltin.

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