TRIS(TRIETHYLSILYL)ANTIMONY AND RELATED COMPOUNDS

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(Received February 26th, 1966)

Very little work has been published lately on the preparation of organometallic compounds with Si–Sb, Sn–Sb, Sn–Bi and similar groups. AMBERGER AND SALAZAR have synthesized tris(trimethylsilyl)antimony and its Ge- and Sn-analogs by the reaction of trilithium antimonide, Li_3Sb, with the trimethylhalogen compounds of silicon, germanium and tin[1]. Organometallic compounds with Sn–Sb and Sn–Bi bonds were obtained with good yields[2] by the interaction of $SbCl_3$ (or $BiCl_3$) and triphenyl-stannyllithium in tetrahydrofuran.

Compounds such as $(C_6H_5)_2Sb–SnR_3$ have been prepared by mixing stoichio-metric amounts of $(C_6H_5)_2SbNa$ and trialkyltin bromides in liquid ammonia[3]. The reaction of chlorotrimethylsilane with di-n-butylantimonymagnesium gives trimethyl-silyldi-n-butylantimony[4]. In all cases, the halides of the corresponding metal (Li, Na, Mg) are formed together with the organometallic compounds.

In this paper we report the novel synthesis of tris(triethylsilyl)antimony and related compounds (Ia–f) by the reaction of the triethyl hydrides of the IV^B group elements with triethyl-antimony or -bismuth in the absence of oxygen*

$$3 (C_2H_5)_3MH + (C_2H_5)_3M' \rightarrow 3 C_2H_6 + [(C_2H_5)_3M]_3M' \text{ (Ia–f)} \qquad (1)$$
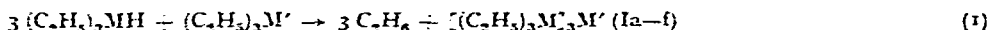
(Ia) $M=Si$, $M'=Sb$; (Ib) $M=Ge$, $M'=Sb$; (Ic) $M=Sn$, $M'=Sb$;

(Id) $M=Si$, $M'=Bi$; (Ie) $M=Ge$, $M'=Bi$; (If) $M=Sn$, $M'=Bi$.

The results obtained are summarized in Table 1.

Some organometallic compounds can be prepared in a similar way if the ethyl derivatives of mercury[6–9], cadmium[10–12], zinc[13], thallium[14], and selenium[15] are used instead of $(C_2H_5)_3M'$.
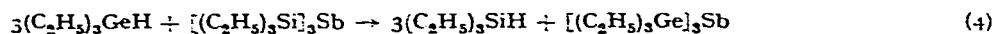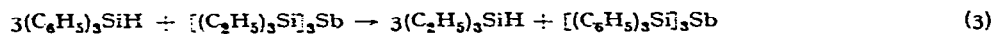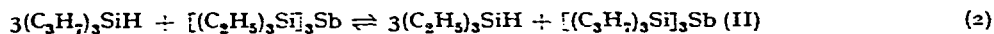
Reaction (1) proceeds in usually good yield in 8.5–20 h at temperatures between 100 and 230°, depending on the nature of the reactants. In this reaction, the reactivity of triethylbismuth is greater than triethylantimony. The results, shown in Table 1, indicate the following order of efficiency of the hydrides:

$$(C_2H_5)_3SnH > (C_2H_5)_3GeH > (C_6H_5)_3SiH > (C_3H_7)_3SiH \simeq (C_2H_5)_3SiH$$
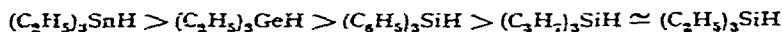
The correctness of this order of the hydrides is proved by reactions (2)–(5). It was found that the triethylsilyl group can be replaced by a triphenylsilyl (eqn. (3)), triethylgermyl (eqn. (4)) or triethylstannyl (eqn. (5)) group. Reaction (2) is reversible and hence triethylsilane and tri-n-propylsilane have the same reactivity. Tris(tri-

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* Short communication, see ref. 5.

n-propylsilyl)antimony (II) in its pure form is more easily obtained by reaction (1) from tri-n-propylsilane and triethylantimony.

$$3(C_3H_7)_3SiH + [(C_2H_5)_3Si]_3Sb \rightleftharpoons 3(C_2H_5)_3SiH + [(C_3H_7)_3Si]_3Sb \text{ (II)} \qquad (2)$$

$$3(C_6H_5)_3SiH + [(C_2H_5)_3Si]_3Sb \rightarrow 3(C_2H_5)_3SiH + [(C_6H_5)_3Si]_3Sb \qquad (3)$$

$$3(C_2H_5)_3GeH + [(C_2H_5)_3Si]_3Sb \rightarrow 3(C_2H_5)_3SiH + [(C_2H_5)_3Ge]_3Sb \qquad (4)$$

$$3(C_2H_5)_3SnH + [(C_2H_5)_3Ge]_3M' \rightarrow 3(C_2H_5)_3GeH + [(C_2H_5)_3Sn]_3M' \qquad (5)$$
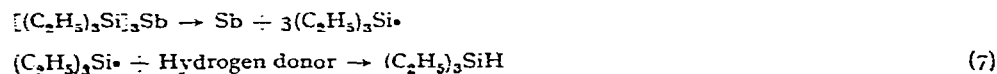$$M' = Sb, Bi$$

Reaction (5) between triethyltin hydride and tris(triethylgermyl)bismuth is carried out at about 170° but under these conditions the tris(triethylstannyl)bismuth (If) formed decomposes entirely according to eqn. (6).

Compounds (Ia–f) are pale yellow, thermally-stable viscous liquids. They were purified by fractional distillation under reduced pressure in nitrogen. Experiments have shown that the thermal decomposition of (Ia–f) in the absence of oxygen proceeds with homolytic cleavage of the M–M'–M bonds. The strength of M–M' bonds decreases in the order Si–Sb $\simeq$ Ge–Sb > Si–Bi $\simeq$ Ge–Bi > Sn–Sb > Sn–Bi (Table 1). The mechanism of the thermal decomposition depends on the structure of (Ia–f).

Tris(triethylstannyl)bismuth (If) is probably decomposed *via* the cage recombination of the triethylstannyl radicals. The reaction, which takes place at about 160°, can be summarised by the following equation

$$2[(C_2H_5)_3Sn]_3Bi \rightarrow 2Bi + 3(C_2H_5)_6Sn_2 \qquad (6)$$

Tris(triethylsilyl)antimony decomposes only at 300°. The thermolysis of this compound gives triethylsilane, antimony in almost quantitative yield and a complex mixture of high-boiling organic silicon compounds. These products indicate the initial formation of such radicals as $(C_2H_5)_3Si\cdot$, which react with the environment

$$[(C_2H_5)_3Si]_3Sb \rightarrow Sb + 3(C_2H_5)_3Si\bullet$$

$$(C_2H_5)_3Si\bullet + \text{Hydrogen donor} \rightarrow (C_2H_5)_3SiH \qquad (7)$$

It is interesting to note that the thermal decomposition of tris(triethylgermyl)-thallium[14] and bis(triethylgermyl)cadmium[10] proceeds under milder conditions of temperature (125–170°) with formation of hexaethyldigermane and free metal as in eqn. (6). Bis(trimethylsilyl)mercury in toluene solution decomposes homolytically. The resulting $(CH_3)_3Si\cdot$ radicals abstracts hydrogen from the solvent molecules[16].

Finally, in the thermal decomposition of tris(triethylstannyl)antimony (Ic) some tin is formed together with metallic antimony which is not surprising because the process proceeds at 220° for 7 h. Under these conditions hexaethylditin can be decomposed[17], as well as the more complex compound with tin–tin bonds. Also should be taken into consideration that a residue of powdered antimony can catalyse the decomposition of organotin compounds. Catalytic quantities of $AlBr_3$ markedly accelerate the decomposition of tris(triethylstannyl)antimony (Ic) and -bismuth (If) which can be described by eqn. (8)

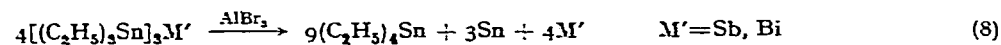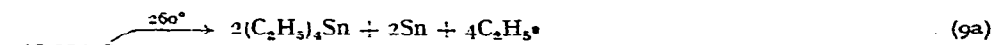$$4[(C_2H_5)_3Sn]_3M' \xrightarrow{AlBr_3} 9(C_2H_5)_4Sn + 3Sn + 4M' \qquad M' = Sb, Bi \qquad (8)$$

TABLE 1

PREPARATION OF TRIS(TRIETHYLSILYL)ANTIMONY AND RELATED COMPOUNDS

| Reagents g (mmole)	Temp. (°C)	Time (h)	Reaction products [(C₂H₅)₃M]₃M'					Analyses		Thermal decomposition		Other products	
			M	M'	Yield (%)	b.p. (°C/mm)	d_4^{20}	Found (%)	Calcd. (%)	Temp. (°C)	Time (h)	Formula	Yield (%)
6.00 (54) (C₂H₅)₃SiH, 3.30 (16) (C₂H₅)₃Sb	230	20	Si	Sb	36.5	148–153/1	1.699	Sb 25.90	Sb 26.04	300	24.5	C_2H_6	95.3
8.75 (54) (C₂H₅)₃GeH, 3.53 (17) (C₂H₅)₃Sb	200	15	Ge	Sb	74.6	157–161/1	1.392	C 36.24 H 7.59	C 35.96 H 7.55	280	33[a]	C_2H_6	99.6
12.08 (61) (C₂H₅)₃SnH, 3.92 (19) (C₂H₅)₃Sb	170	12	Sn	Sb	83.6	174–177/1.5	1.615	C 30.28 H 6.51	C 29.24 H 6.13	220	7	C_2H_6	100
6.09 (52) (C₂H₅)₃SiH, 5.20 (17) (C₂H₅)₃Bi	165–170	15	Si	Bi	32.6	145–146/1	1.273	Bi 37.08	Bi 37.68	290	8	C_2H_6	97.0
6.36 (39) (C₂H₅)₃GeH, 3.50 (12) (C₂H₅)₃Bi	140–145	8.5	Ge	Bi	55.1	167–168/2.5	1.580	Bi 30.31	Bi 30.36	270	21	C_2H_6	79.6
7.01 (38) (C₂H₅)₃SnH, 3.19 (11) (C₂H₅)₃Bi	100	10	Sn	Bi	69.6	...	1.743	Bi 26.11	Bi 25.28	160–165	7	C_2H_6	85
8.38 (53) (C₂H₅)₃SiH, 3.38 (16) (C₂H₅)₃Sb	230	20	Si	Sb	36.0	161–165/1	1.668	C 54.91 H 10.84	C 54.61 H 10.09	...	...	C_2H_6	92.7
2.93 (18) (C₂H₅)₃GeH, 3.02 (6) [(C₂H₅)₃Si]₃Sb	230	16	Ge	Sb	59.1	164–167/2.5	1.386	C 36.12 H 7.51	C 35.96 H 7.55	...	...	(C₂H₅)₃SiH	68.3
2.00 (12) (C₂H₅)₃GeH, 2.28 (4) [(C₂H₅)₃Si]₃Bi	180	16	Ge	Bi	72.8	164–168/2.5	1.583	...	...	...	...	(C₂H₅)₃SiH	98.0
3.90 (19) (C₂H₅)₃SnH, 3.63 (6) [(C₂H₅)₃Ge]₃Sb	180	10	Sn	Sb	81.3	174–176/2	1.615	...	...	...	...	(C₂H₅)₃GeH	88.3
2.46 (12) (C₂H₅)₃SnH, 2.73 (4) [(C₂H₅)₃Ge]₃Bi	170	12	Sn	Bi	0.00	...	...	...	...	...	...	Bi / (C₂H₅)₃Sn / (C₂H₅)₃GeH	89.0 / 83.5 / 61.5

[a] Metallic antimony was obtained in 38.0 % yield. In other experiments, yields of free metals (Sb or Bi) were 100 % of the theoretical quantity.

We have already shown[17] that the addition of small amounts of $AlCl_3$ sharply changes the mechanism and temperature conditions of the decomposition of hexaethylditin

$$2(C_2H_5)_6Sn_2 \quad \xrightarrow{\ 260°\ } \quad 2(C_2H_5)_4Sn + 2Sn + 4C_2H_5 \bullet \tag{9a}$$

$$\xrightarrow[100°]{\ AlCl_3\ } \quad 3(C_2H_5)_4Sn + Sn \tag{9b}$$

Reactions (8) and (9b) seem to have many features in common.

The organometallic compounds (Ia–f) are very reactive. They take part in a number of reactions, all of which involve the breaking of an M–M' bond. They are extremely sensitive to oxygen, rapid oxidation being followed by the disappearance of colour. Tris(triethylsilyl)antimony (Ia) in hexane solution is oxidized by molecular oxygen at 20° to bis(triethylsilyloxy)triethylsilylantimony(III).

$$[(C_2H_5)_3Si]_3Sb + O_2 \rightarrow [(C_2H_5)_3SiO]_2SbSi(C_2H_5)_3 \tag{10}$$
$$(III)$$
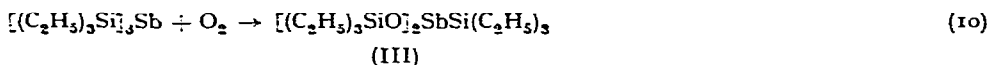
In contrast to reaction (10), oxidation of bis(triethylgermyl)mercury[6], bis-(triethylsilyl)mercury[7] and bis(triethylgermyl)cadmium[10] under the same conditions, gives a mixture of a free metal and an oxide

$$2[(C_2H_5)_3M]_2M' + O_2 \rightarrow 2M' + 2[(C_2H_5)_3M]_2O \tag{11}$$
$$M = Si, Ge; M' = Hg \text{ or } M = Ge, M' = Cd$$
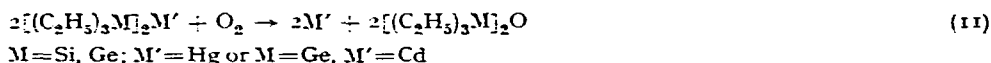
The reactions of tris(triethylsilyl)antimony (Ia) and related compounds with benzoyl peroxide in benzene solution are very exothermic and proceed rapidly at or below room temperature with cleavage of the M–M'–M bonds (Table 2)

$$2[(C_2H_5)_3M]_3M' + 3(C_6H_5COO)_2 \rightarrow 2M' + 6(C_2H_5)_3MOCOC_6H_5 \tag{12}$$
$$M = Si, Ge, Sn; M' = Sb, Bi$$
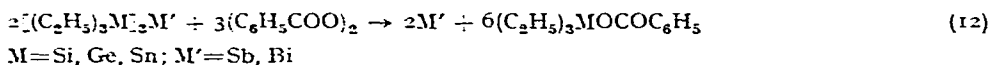
It is suggested that these reactions proceed through a cyclic intermediate adduct which breaks down homolytically. This assumption is proved by the low temperature (5–20°) at which these reactions take place and the absence of by-products. The interaction of benzoyl peroxide and bis(triethylgermyl)mercury[6], bis(triethylgermyl)-cadmium[10], bis(triethylsilyl)cadmium[11] and tris(triethylgermyl)thallium[14] proceeds in the same manner. In these last reactions, however, on account of the interaction of the metal with peroxide, cadmium benzoate and thallium monobenzoate are formed instead of metallic cadmium and thallium.

Compounds of type I react with 1,2-dibromoethane at 95–100° at which temperature the starting materials themselves are quite stable. In this reaction, 1,2-dibromoethane behaves as a mild brominating agent, cleaving the Si–Sb (or Si–Bi, Ge–Bi) bond with simultaneous formation of ethylene (Table 2). The yields of the products are nearly quantitative; there are no by-products.

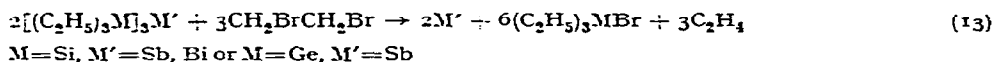$$2[(C_2H_5)_3M]_3M' + 3CH_2BrCH_2Br \rightarrow 2M' + 6(C_2H_5)_3MBr + 3C_2H_4 \tag{13}$$
$$M = Si, M' = Sb, Bi \text{ or } M = Ge, M' = Sb$$

TABLE 2

REACTIONS OF $[(C_2H_5)_3M]_3M'$ (I) WITH BENZOYL PEROXIDE AND 1,2-DIBROMOETHANE

| Reagents taken (g)	Solvent (ml)	Temp. (°C)	Time (min)	Reaction products Yield (%)
1.00 Bz₂O₂; 1.28 (I) (M = Si; M' = Sb)	benzene 10	5–7	5–7	99.7 Sb, 87.0 $(C_2H_5)_3SiOCOC_6H_5$
1.20 Bz₂O₂; 2.37 (I) (M = Sn; M' = Sb)	benzene 10	5–7	5–7	90.8 Sb, 100 $(C_2H_5)_3SnOCOC_6H_5$
3.63 Bz₂O₂; 5.55 (I) (M = Si; M' = Bi)	benzene 20	15–20	7–10	91.8 Bi, 67.4 $(C_2H_5)_3SiOCOC_6H_5$
0.72 Bz₂O₂; 1.66 (I) (M = Ge; M' = Bi)	benzene 12	15–20	3–5	87.2 Bi, 38.4 $(C_2H_5)_3GeOCOC_6H_5$
1.07 Bz₂O₂; 2.44 (I) (M = Sn; M' = Bi)	benzene 10	5–7	5–7	100 Bi, 87.0 $(C_2H_5)_3SnOCOC_6H_5$
1.69 (I) (M = Si; M' = Sb); 5.45 C₂H₄Br₂	—	100	30	100 Bi, 97.0 C₂H₄, 44.9 $(C_2H_5)_3SiBr$
2.30 (I) (M = Ge; M' = Sb); 4.81 C₂H₄Br₂	—	100	30	100 Sb, 98.5 C₂H₄, 100 $(C_2H_5)_3GeBr$
1.45 (I) (M = Si; M' = Bi); 4.36 C₂H₄Br₂	—	40	45	99.0 Bi, 65.7 C₂H₄, 57.5 $(C_2H_5)_3SiBr$

TABLE 3

REACTIONS OF $[(C_2H_5)_3M]_3Sb$ (I) WITH MONOBROMO DERIVATIVES

Reagents taken (g)	Temp. (°C)	Time (h)	Reaction products. Yield (%)	
			$(C_2H_5)_3MBr$	R_3Sb
1.92 (I) (M = Ge); 1.72 C₆H₅CH₂Br	100	1.5	53.7	57.1 R = C₆H₅CH₂[c]
3.77 (I) (M = Sn); 2.70 C₆H₅CH₂Br	100	1.5	86.0	62.2 R = C₆H₅CH₂[a]
3.42 (I) (M = Ge); 2.60 cyclo-C₅H₉Br	160	9	80.0	65.7 R = cyclo-C₅H₉[b]
5.43 (I) (M = Sn); 3.40 cyclo-C₅H₉Br	150	3	81.7	75.0 R = cyclo-C₅H₉[b,c]
1.80 (I) (M = Ge); 3.90 C₆H₅Br	30 hr[e]	70	52.6	49.0 R = C₆H₅[c,d]

[a] The structure of the compound was confirmed by bromination; tribenzylantimony dibromide was isolated, m.p. 106–108°. (Found: Br, 28.83. $C_{21}H_{21}Br_2Sb$ calcd.: Br, 28.80%). [b] B.p. 109–114° at 1.5 mm. d_4^{20} 1.293. Tricyclopentylantimony dibromide, m.p. 104–106°. (Found: C, 37.04; H, 5.27. $C_{15}H_{27}Br_2Sb$ calcd.: C, 36.84; H, 5.57%). [c] Traces of metallic antimony were obtained. [d] M.p. 51–52°; triphenylantimony dibromide, m.p. 214–215 °. No depression of the m.p. was caused by mixing the sample with the pure substance. [e] The lamp used was PRK-2, the distance to the source was 15–17 cm. Irradiation was carried out in a Pyrex ampoule.

The interaction of bis(triethylgermyl)- or bis(triethylstannyl)antimony with alkyl bromides in the absence of a solvent may be represented by the equation

$$[(C_2H_5)_3M]_3Sb + 3RBr \rightarrow 3(C_2H_5)_3MBr + R_3Sb \qquad (14)$$

$$M = Ge, Sn; R = C_6H_5CH_2, cyclo\text{-}C_5H_9$$
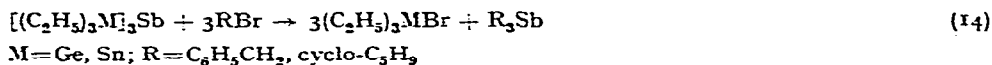
The experimental results are presented in Table 3. It is well known that organometallic compounds of antimony, like R_3Sb, react with alkyl halides, the antimony being converted into the pentavalent state. In our case, the metal has kept the three-valent state. The formation of $(C_2H_5)_3MBr$ and R_3Sb probably occurs as a homolytic reaction, in which truly free radicals are not involved.

Bis(triethylgermyl)mercury reacts with alkyl bromides in the same manner under ultraviolet light[6,7]. We have shown that reaction (14) can be used for the synthesis of asymmetric organometallic compounds containing Ge–Sb bonds, by interchange of radicals between the reactants

$$[(C_2H_5)_3Ge]_3Sb + C_6H_5CH_2Br \rightarrow [(C_2H_5)_3Ge]_2SbCH_2C_6H_5 + (C_2H_5)_3GeBr \qquad (15)$$
$$(IV)$$
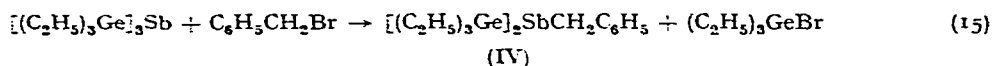
Bis(triethylgermyl)benzylantimony (IV) is a viscous, pale yellow liquid. It is soluble in ordinary organic solvents and relatively stable towards thermal decomposition. It is extremely sensitive to oxidation.

Tris(triethylgermyl)bismuth (Ie) reacts with glacial acetic acid according to the equation

$$2[(C_2H_5)_3Ge]_3Bi + 3CH_3COOH \rightarrow 2Bi + 3(C_2H_5)_3GeOCOCH_3 + 3(C_2H_5)_3GeH \qquad (16)$$
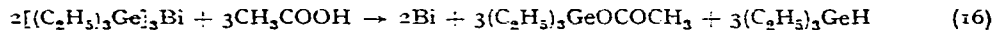
The yields of bismuth, triethylgermane and triethylacetoxygermane are 86.4, 53.4 and 68.7 %, respectively.

EXPERIMENTAL

Procedure

The reactions were carried out in evacuated and sealed apparatus or ampoules. The starting materials were mixed and the products separated and identified without contact with oxygen or air in a special preliminary-evacuated apparatus. Our procedure usually consisted of the following operations.

a. Preparation of starting reagents. A calculated amount of freshly distilled (or freshly recrystallized) substance was placed in an ampoule and, if necessary, a solvent added. The contents of the ampoule were de-gassed by double freezing in liquid nitrogen and re-freezing *in vacuo*. After out-gassing, the ampoule was sealed off.

Easily oxidized starting reagents (for example, triethylantimony) were purified from the oxidized products by careful fractionation *in vacuo* in nitrogen. In this case, graduated ampoules were used as receivers (Fig. 1) and were sealed off when they were full without interruption of the distillation.

b. The preparation of the initial mixtures. The ampoule (A), containing the calculated amount of an initial reagent, was connected to the apparatus by a rubber tube (B), as shown in Fig. 2. Previously, a notch had been made by a glass knife on the breakable tip of the ampoule. After evacuation, stopcock (C) was closed. The tip

of the ampoule (A) was broken and the contents poured into the apparatus. The ampoule (A) was replaced by another, which contained a second component of the reaction. In the moment of replacing, tube (B) was clamped and the apparatus was again evacuated. The apparatus was then sealed off at (D) and the mixture distributed among the ampoules (E) which were then sealed off from the manifold, at the constrictions.

c. *Isolation of gaseous products.* The ampoules (E) were placed in a thermostatted oil bath. After completion of the reaction, each ampoule (E) was immersed in liquid nitrogen. These operations were carried out with tongs behind a safety shield. One by one the frozen ampoules were attached by means of a rubber tube to a gas burette. Previously, the rubber tube and part of the burette had been filled with pure nitrogen. The breakable tip of the ampoule was broken and the reaction mixture allowed to melt. The amount of gaseous products was measured by the change in level of the liquid in the burette. Ampoule (E) was sealed off without being disconnected from the burette. This allowed the gaseous products to be separated from the liquid products without contact with the oxygen of the air. The contents of the burette were analysed by gas chromatography.

d. *Separation of liquid products.* The reaction mixture was poured from the ampoules (E) into the evacuated apparatus shown in Fig. 3, using the method described in "b". The apparatus was re-evacuated and sealed at (F). The volatiles were removed from the reaction mixture, into a trap (G), by cooling the trap with liquid nitrogen while heating compartment (H) slowly (during 3 h) to 100° and maintaining at that temperature for 2 h. The volatiles were then frozen with liquid nitrogen and trap (G) sealed off at (K). The residue was poured from compartment (H) into an evacuated (0.5–1 mm) distillation apparatus. For this purpose a Claisen flask, shown in Fig. 1, was equipped with an inlet tube (L). The receivers in the apparatus were graduated ampoules (M), which were sealed off without interrupting the vacuum distillation.
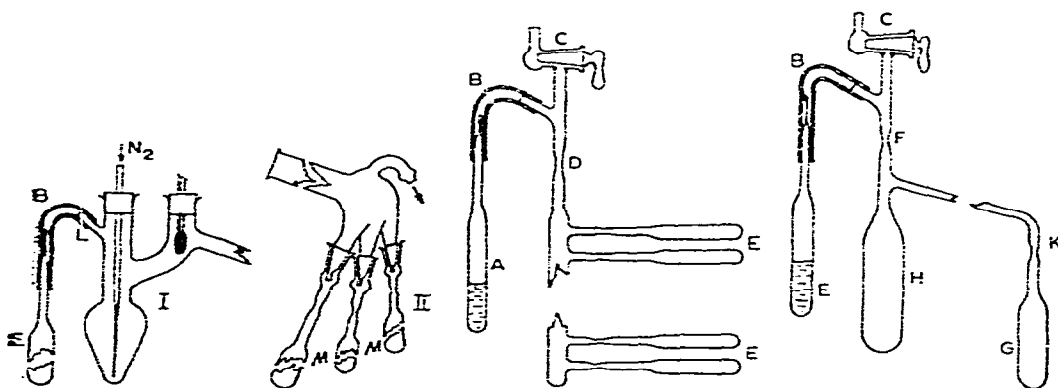

Fig. 1, 2, 3. Claisen flask (I) and receivers (II).

Tris(triethylsilyl)antimony (Ia)

A mixture of 6.00 g (0.052 mole) of triethylsilane and 3.30 g (0.016 mole) of triethylantimony was heated to 230° by means of an oil bath for 20 h. A work-up in

the usual manner gave 1010 ml (95.3 %) of ethane and 2.70 g (36.5 %) of (Ia), b.p. 148–153° at 1 mm. (Found: Sb, 25.90. $C_{18}H_{45}SbSi_3$ calcd.: Sb, 26.04 %).

Reaction of tris(triethylgermyl)antimony (Ib) with triethyltin hydride

In a 10-ml evacuated ampoule, 3.90 g (0.019 mole) of triethyltin hydride and 3.63 g (0.006 mole) of (Ib) were heated for 10 h at 180°. The volatiles were removed from the reaction mixture by re-condensation and distilled under reduced pressure. 2.57 g (88.3 %) of triethylgermane was collected, b.p. 57–60° at 83 mm, n_D^{20} 1.4330. Distillation of the residue in vacuo yielded 3.60 g (81.3 %) of tris(triethylstannyl)-antimony (Ic), b.p. 174–177° at 2 mm, d_4^{20} 1.615.

The other reactions of this type were carried out in a similar way. The results are shown in Table 1.

Disproportionation of tris(triethylstannyl)antimony (Ic)

A mixture of 2.0045 g (0.00271 mole) of (Ic) and 0.0473 g (0.00018 mole) of anhydrous $AlBr_3$ was thermostatted at 150° for 7 h. The reaction mixture was extracted three times with ether. Distillation of the extract gave 1.3204 g (92.1 %) of tetraethyltin, having the characteristic odour of triethyltin chloride, b.p. 77–79° at 13 mm, n_D^{20} 1.4701 (literature[18], b.p. 78° at 13 mm, n_D^{20} 1.4691).

In addition, 0.5703 g (99.8 %) of metallic precipitate containing 42.10 % of tin and 57.90 % of antimony was obtained.

Thermal decomposition of tris(triethylstannyl)bismuth (If)

In a 10-ml ampoule, 3.04 g (0.004 mole) of (If) was heated to 160–170° for 6 h. The metallic bismuth was filtered off, washed with ether and dried at 100° to constant weight yielding 0.77 g (100 %). By distillation in vacuo, 0.97 g (42.7 %) of hexaethyl-ditin was obtained, b.p. 158–160° at 23 mm, n_D^{20} 1.5410 (literature[19], b.p. 161–162° at 23 mm, n_D^{20} 1.5377). The product, in accordance with ref. 20, was disproportionated at 120° in the presence of 2–3 % w/w of $AlCl_3$. Theoretical amounts of metallic tin (0.14 g) and tetraethyltin (0.83 g) were obtained.

Reaction of tris(triethylstannyl)bismuth (If) with benzoyl peroxide

To an anhydrous solution of 1.07 g (0.004 mole) of benzoyl peroxide in 10 ml benzene, frozen in an evacuated apparatus (Fig. 3) cooled with liquid nitrogen, was added in the usual way, 2.44 g (0.003 mole) of (If). The apparatus was sealed off at (F). The components were allowed to melt and to mix. The exothermal reaction was finished after 5–7 min at 5–7°. The benzene solution was decanted from the metallic bismuth (0.62 g, 100 %) into section (G) and the benzene recondensed from section (G) into section (H). The operations described above were repeated 3 times and then section (G) was sealed at (K). Removal of the solvent from the benzene solution left a viscous residue, which was distilled. 2.51 g (87.0 %) of triethyltin benzoate was isolated, b.p. 130–140° at 1 mm, m.p. 78°. No depression of the m.p. was caused by mixing the sample with the pure substance.

The other experiments of this type are shown in Table 2.

Reaction of tris(triethylgermyl)antimony (Ib) with 1,2-dibromoethane

A solution of 2.30 g (0.004 mole) of (Ib) in 4.81 g (0.026 mole) of 1,2-dibromo-

ethane was heated at 100° for 30 min in a 15-ml evacuated ampoule. The usual work-up gave 0.47 g (100 %) of antimony, 127 ml (98.5 %) of ethylene and 2.75 g (100 %) of triethylbromogermane, b.p. 188–191°, n_D^{20} 1.4860 (literature[21], b.p. 190.9° at 760 mm, n_D^{20} 1.4862).

The other experiments of this type are shown in Table 2.

Reaction of tris(triethylgermyl)antimony (Ib) with benzyl bromide (1:1 molar ratio)

A mixture of 5.66 g (0.009 mole) of (Ib) and 1.64 g (0.009 mole) of benzyl bromide was heated at 100° for 30 min. Distillation gave 1.98 g (88.0 %) of triethyl-bromogermane, b.p. 186–189°, n_D^{20} 1.4874 and 2.95 g (58.9 %) of bis(triethylgermyl)-benzylantimony (IV), b.p. 155–159° at 1.5 mm, n_D^{20} 1.5979, d_4^{20} 1.379. (Found: C, 41.66; H, 7.19. $C_{19}H_{37}Ge_2Sb$ calcd.: C, 42.86; H, 7.00 %).

The analytical data suggest that (IV) undergoes some disproportionation during distillation. For other reactions of this series see Table 3.

Reaction of bis(triethylgermyl)mercury with glacial acetic acid

A mixture of 4.04 g (0.008 mole) of bis(triethylgermyl)mercury and 1 ml of glacial CH_3COOH in a 15-ml evacuated ampoule was heated to 130–140° for 1 h. Metallic mercury (1.56 g, 100 %) was precipitated from the solution. Fractionation of the reaction products gave 0.77 g (61.8 %) of triethylgermane, b.p. 120–124°, n_D^{20} 1.4354 (literature[21], b.p. 124° at 760 mm, n_D^{20} 1.4382) and 0.80 g (46.8 %) triethyl-acetoxygermane, b.p. 189–191°, n_D^{20} 1.4370. (Found: CH_3COO, 27.35. $C_8H_{18}GeO_2$ calcd.: CH_3COO, 26.98 %.)

Similarly, treatment of tris(triethylgermyl)bismuth (Ie) with excess glacial acetic acid at 170° for 2 h afforded metallic bismuth, triethylgermane and triethyl-acetoxygermane. The yields were 86.4, 53.4 and 68.7 %, respectively.

Oxidation of tris(triethylsilyl)antimony (Ia)

A solution of 5.05 g (0.011 mole) of (Ia) in 15 ml of dry n-hexane was placed in an ampoule. The ampoule was connected to a burette filled with oxygen. A strong ab-sorption of oxygen (308 ml, 0.014 mole) was observed at 20° for 10 min. The reaction mixture remained homogeneous. By double distillation in vacuum, 3.10 g (57.5 %) of bis(triethylsilyloxy)triethylsilylantimony (III) was obtained, b.p. 134–139° at 1 mm, n_D^{20} 1.4655, d_4^{20} 1.093. (Found: C, 43.22; H, 9.07. $C_{18}H_{45}O_2SbSi_3$ calcd.: C, 43.27; H, 9.07 %.)

SUMMARY

Organometallic compounds of the type $[(C_2H_5)_3M]_3M'$ with M = Si, Ge, Sn and M' = Sb, Bi, are prepared by the reaction of triethylsilane, triethylgermane or tri-ethyltin hydride with triethylantimony or triethylbismuth. These new compounds react with molecular oxygen, benzoyl peroxide, 1,2-dibromoethane, alkyl bromides and other reagents with cleavage of M–M'–M bonds. Their thermal decomposition proceeds in a similar manner.

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