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Abstract

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Homolytic Reactions of Organogermanium and Organosilicon Mercury Compounds

We previously showed (¹) that triethylgermane reacts smoothly with diethylmercury to form bis-(triethylgermyl)-mercury:

$$2(C_2H_5)_3GeH + (C_2H_5)_2Hg \to 2C_2H_6 + (C_2H_5)_3GeHgGe(C_2H_5)_3. \quad (1)$$

In contrast, the reaction of triethylsilane with diethylmercury proceeds slowly (117 hours at 130–140°) and more complexly. Its products are ethyl-(triethylsilyl)-mercury, bis-(triethylsilyl)-mercury, and metallic mercury, isolated in yields of 14.6, 3.3, and 16.8%, respectively.

The primary product of the reaction is apparently ethyl-(triethylsilyl)-mercury:

$$(C_2H_5)_3SiH + (C_2H_5)_2Hg \to C_2H_6 + (C_2H_5)_3SiHgC_2H_5. \quad (2)$$

This is followed by symmetrization of this substance or its interaction with triethylsilane. This process proceeds at a low rate, which is reflected in the yield of bis-(triethylsilyl)-mercury. Metallic mercury arises from decomposition of the initial and/or the mercury compounds formed.

Organosilicon mercury compounds have not so far been isolated in the individual state (²). Their reactivity has practically not been studied. We have found that the substances obtained are unstable toward ultraviolet light (PRK-7 lamp) even when they are in ampoules made of molybdenum glass. Their decomposition proceeds according to equations (3) and (4), with quantitative yields of mercury and hexaethyldisilane. We used this property for analysis of the substances for mercury content.

$$2C_2H_5HgSi(C_2H_5)_3 \xrightarrow{h\nu} 2Hg + (C_2H_5)_6Si_2 + 2C_2H_5, \quad (3)$$

$$(C_2H_5)_3SiHgSi(C_2H_5)_3 \xrightarrow{h\nu} Hg + (C_2H_5)_6Si_2. \quad (4)$$

In addition, these compounds are readily oxidized. For bis-(triethylsilyl)-mercury this reaction is described by equation (5):

$$(C_2H_5)_3SiHgSi(C_2H_5)_3 + O_2 \rightarrow (C_2H_5)_3SiOSi(C_2H_5)_3 + 2Hg. \qquad (5)$$

Oxidation of ethyl-(triethylsilyl)-mercury is accompanied by formation of metallic mercury (yield 43.9%), diethylmercury, and hexaethyldisiloxane. It is highly probable that the oxidative process here is preceded by a symmetrization reaction. As a result, the mixture contains diethylmercury and oxidation products of bis-(triethylsilyl)-mercury (see equation 5).

A similar phenomenon is observed in the interaction of ethyl-(triethylsilyl)-mercury with an equimolar amount of benzoyl peroxide. In this case, 37.7% of the benzoyl peroxide is recovered unchanged. In addition, the reaction mixture contains benzoyloxytriethylsilane, metallic mercury, and diethylmercury, which is difficult to isolate quantitatively.

The yields of the products are, respectively, 100.0, 80.0, and 12.8% of those calculated according to the equation:

$$2C_2H_5HgSi(C_2H_5)_3+(C_6H_5COO)_2 \rightarrow (C_2H_5)_2Hg+Hg+2(C_2H_5)_3SiOCOC_6H_5. \qquad (6)$$

Judging from the data presented, the properties of bis(triethylsilyl)mercury and its germanium analogue (1) coincide. This makes it possible to use the more readily available bis(triethylgermyl)mercury to study the reactivity of compounds of this type.

We have established that the photochemical decomposition of solutions of bis(triethylgermyl)mercury in cumene, tetraethyllead, and tert-butyl peroxide in evacuated ampoules made of molybdenum glass proceeds according to an equation analogous to (4). The yields of mercury and hexaethyldigermane are quantitative in all cases. The solvents, including tert-butyl peroxide, do not undergo induced decomposition. This shows that, under the conditions considered, triethylgermyl radicals are not characterized by reactions involving abstraction of labile hydrogen or cleavage of Sn—C and shielded O—O bonds. Unshielded O—O bonds in benzoyl peroxide (1) or dicyclohexyl percarbonate are cleaved by bis(triethylgermyl)mercury in the dark at room temperature in 3–5 min.

Table 1

Photoreaction of bis(triethylgermyl)mercury (I) with bromo derivatives

Taken into the reaction	Irradiation time, h	$(C_2H_5)_3GeBr$, yield, % of theoretical	R_2Hg, yield, % of theoretical	Hg, yield, % of theoretical
1.69 g I, 2 ml $C_6H_5CH_2Br$	1.0	80.9	62.2; $R = C_6H_5CH_2$	37.8
0.98 g I, 2 ml α-$C_{10}H_7Br$	3.5	55.5	49.0; $R =$ -$C_{10}H_7$	18.6
1.85 g I, 4 ml C_2H_5Br	1.0	56.4	67.0; $R = C_2H_5$	12.0

Note: The reactions were carried out in evacuated ampoules made of molybdenum glass. Distance from the light source (PRK-7 lamp): 12 cm.

The photolysis of bis(triethylgermyl)mercury proceeds quite differently in a medium of α-bromonaphthalene, benzyl bromide, or ethyl bromide. The principal direction of the reactions is described by the equation

$$(C_2H_5)_3GeHgGe(C_2H_5)_3 + 2RBr \rightarrow 2(C_2H_5)_3GeBr + R_2Hg, \tag{7}$$

$$R = \alpha{-}C_{10}H_7,\ C_6H_5CH_2 \text{ and } C_2H_5.$$

Metallic mercury is formed as a side product. The results are summarized in Table 1.

It may be assumed that the primary act of reaction (7) is the interaction of the bromo derivative with bis(triethylgermyl)mercury "in the cage," with homolytic cleavage of the C—Br and Ge—Hg bonds:

$$(C_2H_5)_3GeHgGe(C_2H_5)_3 + RBr \rightarrow (C_2H_5)_3GeHgR + (C_2H_5)_3GeBr. \tag{8}$$

This is then followed by symmetrization of the $(C_2H_5)_3GeHgR$ compound.

In accordance with these ideas, we found that the photochemical reaction of bis(triethylgermyl)mercury with carbon tetrachloride (1) does not initiate a chain free-radical process between CCl_4 and tetraethyllead. As we established earlier, benzoyl peroxide (3) or atmospheric oxygen can serve as initiators of such a process.

At the same time, we found that oxidation of bis(triethylgermyl)mercury in bromobenzene medium causes reaction (7) with $R = C_6H_5$. As a result, along with the oxidation products—triethylgermanium oxide and metallic mercury—

the reaction mixture contains diphenylmercury and triethylbromogermane. The yields of the latter three products are, respectively, 30.5, 68.5, and 26.3%.

When bis(triethylgermyl)mercury is oxidized in a fluorobenzene solution, homolytic cleavage of C—F bonds is not observed. The reaction proceeds according to an equation analogous to (5), with quantitative yields of metallic mercury and triethylgermanium oxide.

Experimental Part

All reactions were carried out under nitrogen or in evacuated sealed ampoules made of molybdenum glass. Photoreactions were initiated with a PRK-7 lamp; the distance to the light source was 12 cm.

Reaction of triethylsilane with diethylmercury. A mixture of 17.39 g of diethylmercury and 15.54 g of triethylsilane (molar ratio 1 : 2) is heated for 117 h to 130–140°. 1.5 liters (100%) of ethane and 2.27 g (16.8%) of mercury are evolved. By threefold fractionation of the mixture in a stream of nitrogen, 3.38 g (14.6%) of ethyl-(triethylsilyl)-mercury is obtained. B.p. 80–85° at 1.5 mm; n_D^{20} 1.4680.

$C_8H_{20}HgSi$. Found %: Hg 58.24
Calculated %: Hg 58.16

A yellowish liquid, depositing mercury on contact with atmospheric oxygen.

In addition, 0.97 g (3.3%) of bis-(triethylsilyl)-mercury is isolated, b.p. 98–100° at 1 mm. A lemon-yellow liquid, readily oxidized with evolution of mercury.

$C_{12}H_{30}HgSi_2$. Found %: Hg 46.63
Calculated %: Hg 46.53

Photodecomposition of ethyl-(triethylsilyl)-mercury. An ampoule containing 0.4314 g of the substance is irradiated for 14 h. 0.2513 g (100%) of mercury and 0.1800 g of liquid with n_D^{20} 1.4740 are obtained. The liquid accumulated in a series of experiments is distilled. B.p. 96–106° at 3.5 mm. Literature data for hexaethyldisilane (4): b.p. 87–89° at 2.5 mm; n_D^{20} 1.4759.

In addition, gaseous products are formed during the reaction; these were not studied in detail.

Under comparable conditions, from 0.5314 g of bis-(triethylsilyl)-mercury, 0.2425 g (98.25%) of mercury and 0.2880 g (100%) of hexaethyldisilane with n_D^{20} 1.4719 are obtained.

Reaction of ethyl-(triethylsilyl)-mercury with benzoyl peroxide. To a solution of 1.06 g of benzoyl peroxide in 8 ml of dry benzene, 1.51 g of ethyl-(triethylsilyl)-mercury is added. The exothermic reaction is complete in 7–10 min. 0.35 g (80.0%) of mercury is evolved. The benzene is removed in vacuo. To the residue, 1 ml of absolute methanol is added. 0.40 g (37.7%) of benzoyl peroxide is precipitated. The melting point of the substance and of a mixed sample is 104-105°. Methanol and volatile products are distilled off in vacuo into a trap cooled with liquid nitrogen.

From the residue, 0.52 g (100%) of benzoic acid, m.p. 120° (from water), is isolated, formed upon methanolysis of triethylsilyl benzoate. Diethylmercury is identified as ethylmercuric iodide. For this purpose, iodine solution is added to the contents of the trap until the color persists. 0.10 g (12.8%) of a substance with m.p. 183-184° is obtained. A mixed sample has the same melting point.

Photodecomposition of bis-(triethylgermyl)-mercury in tetraethyltin. In an ampoule, a solution of 1.36 g of bis-(triethylgermyl)mercury in 4 ml of tetraethyltin is irradiated (3 h). 0.51 g (97.5%) of mercury is evolved. By fractionation in vacuo, unreacted tetraethyltin is isolated, b.p. 62-64° at 10 mm, n_D^{20} 1.4700, and 0.78 g (93.2%) of hexaethyldigermane. B.p. 90-91° at 1 mm; n_D^{20} 1.4958. Literature data (5): b.p. 61-62° at 0.007 mm; n_D^{20} 1.4960. Ethane and ethylene are not formed during the reaction. The test for triethylgermane is negative.

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