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Abstract

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BIS(TRIETHYLGERMYL)MERCURY*—THE FIRST ORGANOGERMANIUM COMPOUND OF MERCURY

Organogermanium compounds with Ge—M bonds (M = a metal of the silicon or lithium subgroup) are known, and their reactivity has been studied fairly well ([1,2]). Recently, after several unsuccessful attempts ([3,4]), compounds with a Ge—Mg bond were synthesized ([5]). The possibility of synthesizing organogermanium derivatives of other metals had not been discussed.

We have shown that, in the interaction of diethylmercury with triethylgermane (molar ratio 1 : 2) in the absence of atmospheric oxygen at 100–120°, bis(triethylgermyl)mercury and ethane are formed in yields of 66.5 and 96.8%, respectively.*

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

Bis(triethylgermyl)mercury is a thermally stable lemon-yellow liquid, distilling in a stream of nitrogen under reduced pressure. When heated to $160 \pm 1^\circ$ in an evacuated ampoule, the substance slowly decomposes with the liberation of mercury. After 19 h, the yield of mercury is only 9.3% of the theoretical amount.

At the same time, bis(triethylgermyl)mercury is very reactive and, on contact with atmospheric oxygen, immediately begins to liberate mercury. The reaction is described exactly by equation (2) and may be used for analyzing the substance for mercury content:

$$2(C_2H_5)_3GeHgGe(C_2H_5)_3 + O_2 \rightarrow 2(C_2H_5)_3GeOGe(C_2H_5)_3 + 2Hg. \quad (2)$$

The interaction of bis(triethylgermyl)mercury with benzoyl peroxide proceeds at room temperature with evolution of heat. It is very probable that the reaction proceeds with intermediate formation of a cyclic complex, which then decomposes homolytically.

$$\text{cyclic complex involving } (C_2H_5)_3Ge,\ Hg,\ Ge(C_2H_5)_3,\ C_6H_5COO,\ OCOC_6H_5 \longrightarrow Hg + 2(C_2H_5)_3GeOCOC_6H_5 \quad (3)$$

The yields of mercury and triethylgermyl benzoyloxide are 94.0 and 86.9%, respectively. In contrast, bis(triethylgermyl)mercury does not react with tert-butyl peroxide either at room temperature for 12 h or at 100° for 1 h. We observed a similar phenomenon earlier in studying hexaethyldistannane: the Sn—Sn bond is cleaved by benzoyl peroxide at ordinary temperature and proves stable to the action of tert-butyl peroxide even under conditions of its decomposition at 130° ([6,7]).

Bis(triethylgermyl)mercury is sensitive to the action of light. Upon irradiation with ultraviolet light (PRK-7 lamp), the substance dissociates along the Ge—Hg bonds even when it is in an ampoule made of molybdenum glass. In this process mercury and hexaethyldigermane are formed quantitatively. The presence of benzene does not alter the course of the reaction.

$$(C_2H_5)_3GeHgGe(C_2H_5)_3 \rightarrow Hg + (C_2H_5)_3Ge—Ge(C_2H_5)_3. \quad (4)$$

* This compound was obtained simultaneously with us by W. Neumann. (Private communication of Dr. Neumann at the XIX IUPAC Congress.)

Since the hexaethyldigermane formed is not decomposed by ultraviolet light, reaction (4) can also be used for analytical purposes.

Photolysis of bis-(triethylgermyl)mercury in carbon tetrachloride proceeds with the formation of metallic mercury and triethylchlorogermane. The yields are, respectively, 60.0 and 36.2%. In addition, hexachloroethane was found in the reaction mixture. Consequently, the reaction follows a free-radical scheme. Moreover, in contrast to true organomercury compounds (*8-10*), products of the type RHgCl do not arise, since both Ge—Hg bonds undergo homolysis.

The photochemical reaction of bis-(triethylgermyl)mercury with bromobenzene proceeds in a very distinctive manner. Its products are triethylbromogermane, diphenylmercury, and metallic mercury, isolated in yields of 69.2, 45.3, and 4.9%, respectively. Since bromobenzene is stable to ultraviolet light, the primary step of the process must be homolysis of one of the two Ge—Hg bonds in bis-(triethylgermyl)mercury. The resulting $(C_2H_5)_3Ge\cdot$ radicals, like triphenylsilyl radicals (*11*), abstract bromine from bromobenzene, while the phenyl radicals thereby formed are trapped by mercury.

Thus, bis-(triethylgermyl)mercury can serve as a source of practically unstudied organogermanium radicals with the radical function at the germanium atom. In addition, bis-(triethylgermyl)mercury may prove to be an extremely interesting model substance for the study of chain free-radical processes initiated by the decomposition of organoelement compounds.

A reaction similar to (1) in the organotin series was studied by us earlier (*12*). It proceeds quantitatively according to the equation

$$2(C_2H_5)_3SnH + (C_2H_5)_2Hg \rightarrow (C_2H_5)_6Sn_2 + 2C_2H_6 + Hg. \quad (5)$$

It is possible that in this case as well bis-(triethylstannyl)mercury is first obtained, which then decomposes according to an equation analogous to (4).

Investigations in this field are continuing.

Experimental Part

All reactions were carried out under nitrogen or in evacuated sealed ampoules.

Bis-(triethylgermyl)mercury. 6.83 g of triethylgermane and 5.50 g of diethylmercury are heated to 100–120° in a vessel equipped with a reflux condenser connected to a gas burette. 920 ml (96.8%) of ethane, identified by the chromatographic method, is collected. The mixture is fractionated in vacuo under a stream of nitrogen. The receivers are ampoules, which are sealed off as the fractions are collected, without interrupting the distillation. 7.34 g (66.5%) of bis-(triethylgermyl)mercury is obtained; b.p. 118–120° at 1.5 mm; n_D^{20} 1.5696.

Found, %: Hg 38.59; 38.62. ($C_{12}H_{30}Ge_2Hg$). Calculated, %: Hg 38.56.

A lemon-yellow liquid, depositing mercury on contact with air.

Oxidation of bis-(triethylgermyl)mercury. An ampoule containing 0.7473 g of bis-(triethylgermyl)mercury is opened and left overnight. The substance absorbs the theoretical amount of oxygen (0.0228 g), with quantitative separation of mercury (0.2865 g) and bis-triethylgermanium oxide (0.4836 g). B.p. 130–132° at 20 mm; n_D^{20} 1.4612, which agrees with the data obtained by independent synthesis.

Photodecomposition of bis-(triethylgermyl)mercury. A Pyrex ampoule containing 2.1397 g of the substance is irradiated with ultraviolet light until decolorization (3 hours; PRK-7 lamp; distance from the light source 12 cm). 0.8268 g (100%) of mercury and 1.3129 g (100%) of hexaethyldigermane are obtained; b.p. 115–116° at 2.5 mm; n_D^{20} 1.4971. Literature data (*14*): b.p. 61–62° at 0.007 mm; n_D^{20} 1.4960.

Reaction of bis(triethylgermyl)mercury with benzoyl peroxide. A solution of 0.82 g of benzoyl peroxide in 7 ml of benzene is frozen, and 1.88 g of bis(triethylgermyl)mercury is added. On thawing, a vigorous exothermic reaction begins, ending in 3–5 min. 0.68 g (94.0%) of mercury is isolated. Fractionation of the mixture gives 1.76 g (86.9%) of triethylgermyl benzoyloxide; b.p. 106–108° at 1.5 mm; n_D^{20} 1.5076. The product is titrated with a NaOH solution using phenolphthalein. Found, %: C_6H_5COO 44.08. $C_{13}H_{20}GeO_2$. Calculated, %: C_6H_5COO 43.11.

Photoreaction of bis(triethylgermyl)mercury with bromobenzene. A solution of 2.65 g of bis(triethylgermyl)mercury in 4 ml of bromobenzene is irradiated in a molybdenum-glass ampoule (PRK-7 lamp, distance from the light source 12 cm) for 2 h. 0.05 g of mercury is isolated. Yield 4.9%. Fractionation in vacuum gives 1.69 g, 69.2%, of triethylbromogermane; b.p. 62–64° at 10 mm; n_D^{20} 1.4918. Literature data ([13]): b.p. 190.9°; n_D^{20} 1.4892. The residue is recrystallized from benzene. 0.82 g (45.3%) of diphenylmercury is isolated. The melting point of the substance and of a mixed sample is 120–122°.

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Note: Figure translations are in progress. See original paper for figures.