N. S. VYAZANKIN, Corresponding Member of the Academy of Sciences of the USSR G. A. RAZUVAEV,

E. N. GLADYSHEV, T. G. GURIKOVA

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Abstract

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**N. S. VYAZANKIN, Corresponding Member of the Academy of Sciences of the USSR G. A. RAZUVAEV,
E. N. GLADYSHEV, T. G. GURIKOVA**

THE FIRST ORGANOMETALLIC COMPOUNDS WITH Si–Si–Hg–AND Si–Hg–Ge GROUPINGS

Recently the possibility has been demonstrated of the existence of organoelement compounds with covalent bonds Ge–Hg–Ge, Si–Hg–Si, Si–Hg–C, Si–Zn–Si, etc. We and, independently of us, Neumann have established that such substances arise in the interaction of triethylgermane ([1]), triethylsilane ([2]), or diphenylgermane ([3]) with diethylmercury. Other methods for the synthesis of similar compounds have been proposed by Wieber and co-workers ([4]).

Continuing this investigation, we found that pentaethyldisilane* reacts with diethylmercury at 155-160° (19 hours) with the formation of substances containing Si–Si–Hg and Si–Si–Hg–Si–Si groupings. The reaction products are ethane, ethyl-(pentaethyldisililyl)-mercury, bis-(pentaethyldisililyl)-mercury, and metallic mercury, isolated in yields of 67.0, 19.5, 8.1, and 12.5%, respectively.

Initially, unsymmetrical ethyl-(pentaethyldisililyl)-mercury is probably formed,

$$(C_2H_5)_3SiSi(C_2H_5)_2H + (C_2H_5)_2Hg \rightarrow C_2H_6 + C_2H_5HgSi(C_2H_5)_2Si(C_2H_5)_3. \tag{1}$$

The very fact of its formation shows that pentaethyldisilane in this reaction is similar to triethylsilane ([2]) and differs from triethylgermane, whose interaction with diethylmercury proceeds with the formation only of symmetrical bis-(triethylgermyl)-mercury ([1]).

Ethyl-(pentaethyldisililyl)-mercury is a pale-yellow liquid, distilling in vacuum without decomposition. B.p. 100-104° at 1 mm; n_D^{20} 1.5353.

Found %: Hg 46.30
$C_{12}H_{30}HgSi_2$. Calculated %: Hg 46.53

Like other compounds of this type, ethyl-(pentaethyldisililyl)-mercury is readily oxidized by air and decomposes under the action of ultraviolet light even when contained in evacuated ampoules made of molybdenum glass. Both processes proceed with quantitative liberation of mercury, which can be used for analytical purposes.

We were unable to obtain the symmetrical reaction product—bis-(pentaethyldisililyl)-mercury—in an analytically pure state. This yellow-orange liquid distills under nitrogen at 180–190° at 1 mm with considerable decomposition. The metallic mercury liberated in this process deposits on the walls of the apparatus. As a result, analysis of the distillate for mercury gives values lower than those calculated for bis-(pentaethyldisililyl)-mercury.

Found %: Hg 30.70
$C_{20}H_{50}HgSi_4$. Calculated %: Hg 33.24

The formation of bis-(pentaethyldisililyl)-mercury can be explained either by symmetrization of ethyl-(pentaethyldisililyl)-mercury or by the interaction of the latter with the starting pentaethyldisilane according to an equation similar to (1).

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* Obtained by reduction of pentaethylbromodisilane (^{6}) with lithium aluminum hydride in an ether medium. Yield 73.5%; b.p. 78–83° at 1.5 mm; n_D^{20} 1.4608. Analysis for hydrogen bound to silicon. Found %: H 0.51, 0.52. $C_{10}H_{26}Si_2$. Calculated %: H 0.50.

The following fact is consistent with the first assumption: ethyl-(triethylsilyl)-mercury, constructed analogously, can undergo symmetrization at elevated temperatures (11 hours at 170°).

$$2C_2H_5HgSi(C_2H_5)_3 \rightarrow (C_2H_5)_2Hg + (C_2H_5)_3SiHgSi(C_2H_5)_3.$$

In this process, along with the starting ethyl-(triethylsilyl)-mercury and metallic mercury, we isolated diethylmercury and bis-(triethylsilyl)-mercury with b.p. 98–100° at 1 mm. The yields were, respectively, 31.3, 18.3, 5.0, and 33.6%. The structures of the substances obtained were confirmed by elemental analysis.

In accordance with the second assumption, we found that ethyl-(triethylsilyl)-mercury and ethyl-(pentaethyldisilyl)-mercury react with triethylgermane and triethyltin hydride with formation of ethane. In the case of triethylgermane, the process of substitution of the ethyl group bound to mercury by a triethylgermyl residue proceeds very smoothly under comparatively mild conditions (1–2 hours at 100°)

$$(C_2H_5)_3GeH + C_2H_5HgR \rightarrow C_2H_6 + (C_2H_5)_3GeHgR,$$

$$R = (C_2H_5)_3Si \text{ and } (C_2H_5)_3SiSi(C_2H_5)_2$$

By this route, triethylsilyl-(triethylgermyl)-mercury and pentaethyldisilyl-(triethylgermyl)-mercury have been synthesized—the first organoelement compounds with Si—Hg—Ge and Si—Si—Hg—Ge groupings.

The yield of triethylsilyl-(triethylgermyl)-mercury is 26.2%. It is a lemon-yellow liquid with b.p. 130-131° at 1.5 mm.

$C_{12}H_{30}GeHgSi$.	Found, %:	Hg 42.45
	Calculated, %:	Hg 42.18

Under the action of ultraviolet light (PRK-7 lamp; distance from the light source 12 cm; the substance in an ampoule of molybdenum glass), this compound decomposes after only 2 hours with formation of mercury and triethyl-(triethylgermyl)-silane. The yields are quantitative.

$$(C_2H_5)_3GeHgSi(C_2H_5)_3 \xrightarrow{h\nu} Hg + (C_2H_5)_3Ge\text{—}Si(C_2H_5)_3.$$

Triethyl-(triethylgermyl)-silane has b.p. 92° at 1.5 mm; n_D^{20} 1.4858. Literature data (^{5}): b.p. 254.5°; n_D^{26} 1.4860.

$C_{12}H_{30}GeSi$.	Found, %:	C 53.18; H 11.18
	Calculated, %:	C 52.40; H 11.0

The yield of pentaethyldisilyl-(triethylgermyl)-mercury is 50.4%. It is a yellow-orange liquid. It distills in vacuo in a stream of nitrogen with very slight decomposition. B.p. 159-163° at 1 mm. It is readily oxidized in air with separation of mercury.

$C_{16}H_{40}GeHgSi_2$.	Found, %:	Hg 35.78
	Calculated, %:	Hg 35.71

On the basis of this and previously published work (^{2}), it may be concluded that substances with Si—Hg—C, Si—Si—Hg—C, Si—Hg—Ge, and Si—Si—Hg—Ge groupings are more stable than ordinary unsymmetrical organomercury compounds. In particular, their ability to distill in vacuo without decomposition or symmetrization is noteworthy. At the same time, the symmetrical and unsymmetrical organoelement compounds studied, with Si—Hg and Ge—Hg bonds, unlike ordinary organomercury compounds, are exceptionally sensitive to atmospheric oxygen and to acyl peroxides (^{1},^{2}).

Thus, for example, the interaction of bis-(triethylgermyl)-mercury with an equimolar amount of dicyclohexyl percarbonate in toluene is completed at room temperature in 10 min. The reaction is accurately described by the equation

$$(C_2H_5)_3GeHgGe(C_2H_5)_3 + (C_6H_{11}OCOO)_2 \rightarrow Hg + 2(C_2H_5)_3GeOCOOC_6H_{11}.$$

The yield of mercury is quantitative. The second product is extremely unstable and readily decarboxylates, as may be judged from the gradual appearance of excess pressure in the evacuated sealed reaction vessel after completion of the main reaction:

$$(C_2H_5)_3GeOCOOC_6H_{11} \rightarrow CO_2 + (C_2H_5)_3GeOC_6H_{11}.$$

Yield of triethyl(cyclohexyloxy)germane, 78.5%. B.p. 72–73° at 1.5 mm; n_D^{20} 1.4645.

Found, %: C 57.21; H 10.19
$C_{12}H_{26}GeO$. Calculated, %: C 55.66; H 10.12

Finally, it should be noted that the silicon- and germanium-organic mercury compounds studied are much more sensitive to light than ordinary organomercury compounds.

All operations for the synthesis, purification, and study of the reactivity of the compounds considered above were carried out under a stream of nitrogen or in evacuated sealed ampoules.

Research Institute of Chemistry
at Gorky State University
named after N. I. Lobachevsky

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