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# Chemistry

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**Abstract**

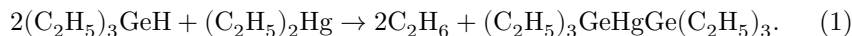
**Full Text**

## **Chemistry**

**N. S. Vyazankin, Corresponding Member of the Academy of Sciences of the USSR G. A. Razuvaev, S. P. Korneva, O. A. Kruglaya, R. F. Galiulina**

### **Reaction of Triethyltin Hydride and Its Analogs with Diethylzinc**

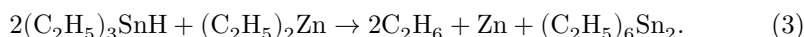
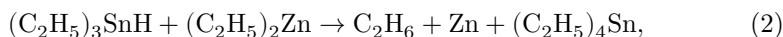
We have previously shown that substances of the type  $(C_2H_5)_3MH$  ( $M = Sn, Ge$  and  $Si$ ) can react with diethylmercury to form bimetallic organometallic compounds (<sup>1,2</sup>). For example:



The reactions of organic zinc derivatives with organoelement hydrides of Group IV have not been studied. It seemed probable, however, that diethylzinc would react with them similarly to its structural analog, diethylmercury.

As the study has shown, when diethylzinc interacts with triethyltin hydride (9 h at 100°), zinc, ethane, tetraethyltin, and hexaethyldistannane are formed. Their yields are respectively 83.5; 54.2; 70.4 and 19.2%.

The reaction apparently proceeds in two directions, of which (2) is predominant:



The interaction of the same hydride with diethylmercury (<sup>3</sup>) proceeds less complexly and is well described by an equation analogous to (3).

For the reaction under discussion, the formation of bimetallic organometallic compounds is not characteristic. However, it may be assumed that zinc and hexaethyldistannane are obtained through decomposition of an intermediate bis-(triethylstannyl)zinc. In agreement with this, we have established that the reactions of diethylzinc with triethylgermane and triethylsilane proceed with the formation of compounds, colored yellow-lemon, containing Ge–Zn–Ge and Si–Zn–Si groupings. In addition, according to equations similar to (2) and (3), tetraethylgermane, hexaethyldigermane, and their Si analogs are formed.

The colored compounds, like bis-(triethylgermyl)mercury (<sup>1,2</sup>), are very sensitive to the action of light and atmospheric oxygen. Their thermal stability is low. In contrast to bis-(triethylgermyl)mercury, they begin to decompose already at 80–90°, with liberation of metallic zinc. In addition, they are nonvolatile and cannot be isolated in the pure state by distillation or recondensation in vacuum. We made use of the nonvolatility of the bimetallic organometallic compounds to separate them from other products in the form of nondistilling colored residues. This made it possible to estimate the yield of the colored substances and to compare their chemical properties with those of bis-(triethylgermyl)mercury.

Thus, for example, in the interaction of diethylzinc with triethylgermane (15 h at 125°), the yield of the nondistilling colored residue reaches 55.4%. The other reaction products are ethane, zinc, and tetraethylger-

germanes, isolated in yields of 94.3, 29.6, and 8.6%. The colored residue is decolorized by water in 3–4 hours at room temperature. In this process zinc hydroxide (yield 58.8%), triethylgermane, pentaethyldigermane, and hexaethyldigermane are formed. In contrast, bis(triethylgermyl)mercury is stable toward water even upon contact for many days.

The colored residue readily reacts with ethyl bromide (2–3 hours at 50°) to form zinc bromide (yield 67.2%), tetraethylgermane, hexaethyldigermane, and, judging from the molecular weight, octaethyltrigermane.

Ethyl bromide reacts quite differently with bis(triethylgermyl)mercury (<sup>2</sup>). In this case it is not bromine that adds to the central atom, but ethyl groups. As a result, diethylmercury and triethylbromogermane are formed.

The colored residue reacts with 1,2-dibromoethane at room temperature with evolution of heat. Along with zinc bromide and ethylene (yields 92.9 and 38.6%), a complex mixture of germanium-containing products is obtained, from which triethylbromogermane can be isolated in low yield (14.0%).

The reaction of bis(triethylgermyl)mercury with dibromoethane is also exothermic, but proceeds more simply and can be described by the equation:



The yields of mercury, ethylene, and triethylbromogermane are respectively 97.4, 74.9, and 57.8%.

Finally, we have found that the colored residue is readily decolorized upon interaction with benzoyl peroxide. The identified products of this exothermic reaction are zinc dibenzoate, triethylbenzoyloxygermane, pentaethylbenzoyloxydigermane, and hexaethyldigermane.

As is known (<sup>1</sup>), bis(triethylgermyl)mercury reacts with an equimolar amount of peroxide to form metallic mercury and triethylbenzoyloxygermane.

On the basis of the material presented, it should be assumed that the colored residue contains not an individual substance, but a mixture of compounds of the series



where  $n = 0, 1, \dots$ , and high-boiling products of their decomposition of the hexaethyldigermene type.

In this case it becomes clear why, under very mild temperature conditions, even under the influence of such reagents as water or benzoyl peroxide, the colored residue gives complex mixtures of products, including compounds with Ge–Ge bonds.

At the same time, the mechanism of formation of compounds of series (A) in the reaction of triethylgermane with diethylzinc remains unclear, all the more so since, under comparable conditions, the same hydride reacts smoothly with diethylmercury according to equation (1).

As may be noted, compounds of series (A) differ substantially in chemical properties from bis(triethylgermyl)mercury. In particular, for them reactions (apart from photolysis and thermolysis) accompanied by liberation of metallic zinc are almost unknown. For bis(triethylgermyl)mercury, reactions proceeding with liberation of free mercury are rather characteristic (interaction with oxygen and acyl peroxides (<sup>1</sup>, <sup>2</sup>), reaction with 1,2-dibromoethane, etc.).

The substances of series (A) also differ from ordinary organozinc compounds. As is known, the interaction of the latter with mercuric sulfide proceeds with formation of organic derivatives of mercury. In the exothermic reaction of mercuric sulfide with colored substances of series (A), compounds with Ge–Hg–Ge groupings do not arise. Its products are mercury, zinc, triethylchlorogermene, and pentaethylchlorodigermene.

The possibility of the formation of compounds with Si–Zn–Si bonds was recently demonstrated by Wiberg and co-workers (<sup>4</sup>). They obtained bis(triphenylsilyl)zinc by the action of triphenylsilylpotassium on zinc chloride in liquid ammonia.

We have established that triethylsilane reacts with diethylzinc only under rather severe conditions (8 h at 160°). In this case, the yield of compounds with Si–Zn–Si groups is only 4.5%. The reaction proceeds toward the formation of metallic zinc (yield 74.3%), tetraethylsilane, and hexaethyldisilane.

## Experimental Part

The reactions were carried out in evacuated sealed ampoules. All operations for preparing the starting mixtures and isolating the bimetalloorganic compounds

were performed in evacuated systems, in special apparatus. Gaseous products were analyzed by a chromatographic method.

**Reaction of triethylgermane with diethylzinc.** 4.86 g of diethylzinc and 12.65 g of triethylgermane are thermostated in ampoules for 15 h at 125°. 1660 ml (94.2%) of ethane and 0.76 g (29.6%) of zinc are liberated. The mixture is decanted from the zinc and gradually heated over 5-6 h to 80° in a sealed evacuated vessel, the outlet of which is cooled with liquid nitrogen. Volatile products are distilled off; by fractionating them, 1.26 g (8.6%) of tetraethylgermane is isolated, b.p. 157-162°;  $n_D^{20}$  1.4429. The yield of the non-distillable residue colored lemon-yellow is 8.41 g (55.4%).

The following reactions are characteristic of the residue:

**Reaction with benzoyl peroxide.** A solution of 3.32 g of benzoyl peroxide in 25 ml of dry benzene is added to 3.62 g of the colored residue. The mixture becomes decolorized with evolution of heat. 1.43 g of zinc dibenzoate crystallizes out and is filtered off. Distillation of the filtrate gives 0.97 g of hexaethyldigermane, b.p. 90-94° at 2.5 mm;  $n_D^{20}$  1.4988, which agrees with literature data <sup>(1)</sup>, and 0.24 g of triethylbenzoyloxygermane, b.p. 113-115° at 3 mm;  $n_D^{20}$  1.5110. Literature data <sup>(5)</sup>: b.p. 290° at 760 mm;  $n_D^{20}$  1.513.

The product is titrated with NaOH solution using phenolphthalein.

$C_{13}H_{20}GeO_2$ .	Found, %:	$C_6H_5COO$ 42.61
	Calculated, %:	$C_6H_5COO$ 43.11

In addition, 0.60 g of pentaethylbenzoyloxydigermane is obtained, b.p. 140-146° at 2 mm;  $n_D^{20}$  1.5287.

$C_{17}H_{30}Ge_2O_2$ .	Found, %:	$C_6H_5COO$ 28.02
	Calculated, %:	$C_6H_5COO$ 29.42

**Reaction with water.** To 6.58 g of the colored residue, 10 ml of water is added. After 3-4 h the organic layer becomes decolorized. 1.00 g of zinc hydroxide is isolated. The organic layer is dried over  $CaCl_2$  and fractionated. 0.40 g of triethylgermane is obtained, b.p. 62-70° at 96 mm;  $n_D^{20}$  1.4361. Literature data <sup>(6)</sup>: b.p. 124° at 760 mm;  $n_D^{20}$  1.4382. In addition, 1.46 g of pentaethyldigermane is isolated, b.p. 115° at 5 mm;  $n_D^{20}$  1.4808, and 2.14 g of hexaethyldigermane, b.p. 88-90° at 2 mm;  $n_D^{20}$  1.4948.

**Reaction with mercuric chloride.** 3.40 g of the colored residue is added to a solution of 2.38 g of mercuric chloride in 25 ml of dry ether. During the exothermic reaction, 1.57 g (89.9%) of mercury and 0.17 g (29.8%) of zinc are liberated. Distillation gives 0.92 g of triethylchlorogermane, b.p. 65-67° at 17 mm;  $n_D^{20}$  1.4575.

$C_6H_{15}GeCl$ .	Found, %:	Cl 17.90
	Calculated, %:	Cl 18.16

In addition, 0.71 g of pentaethylchlorodigermane is obtained, b.p. 120–127° at 17 mm;  $n_D^{23}$  1.5015.

$C_{10}H_{25}Ge_2Cl$ .	Found, %:	Cl 9.79
	Calculated, %:	Cl 10.88

**Reaction of bis-(triethylgermyl)mercury with dibromoethane.** 2.29 g of bis-(triethylgermyl)mercury is added to 3 ml of dibromoethane. The exothermic reaction is complete in 3–5 min. 74 ml (74.9%) of ethylene and 0.86 g (97.4%) of mercury are evolved. On distillation, 1.22 g (57.8%) of triethylbromogermane is isolated, b.p. 75–80° at 18 mm;  $n_D^{20}$  1.4845. Literature data <sup>(6)</sup>: b.p. 190.9° at 760 mm;  $n_D^{20}$  1.4862.

$C_6H_{15}BrGe$ .	Found, %:	Br 32.68
	Calculated, %:	Br 33.34

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