Chemistry

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1964

SovietRxiv

Abstract

Full Text

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BIS-(TRIETHYLGERMYL)-CADMIUM. SYNTHESIS AND PROPERTIES

Recently, methods for obtaining bi- and polymetallic organic compounds have been intensively developed. Substances with Ge—Hg—Ge, Si—Hg—Ge, Si—Hg—Si, and Si—Hg—C groupings arise in the interaction of diethylmercury with triethylgermane ([1]), diphenylgermane ([2]), triethylsilane ([3]), and pentaethyldisilane ([4]). The range of compounds of this kind can evidently be readily expanded by using other Ge- and Si-organic hydrides. Expansion of the synthetic possibilities of the reaction under discussion may also proceed by replacing diethylmercury with its structural analogues.

Thus, for example, we have found that triethylgermane under mild conditions (3 hours at 80—85°) reacts with diethylcadmium with the formation of bis-(triethylgermyl)-cadmium and ethane, the yields of which are 78.6 and 90.3%.

$$2(C_2H_5)_3GeH + (C_2H_5)_2Cd \rightarrow 2C_2H_6 + (C_2H_5)_3GeCdGe(C_2H_5)_3.$$

Bis-(triethylgermyl)-cadmium is a yellow-lemon-colored liquid. In contrast to bis-(triethylgermyl)-mercury ([1]), it is nonvolatile and cannot be isolated in the pure state. The structure of this new bimetallic organic compound, in our opinion, is quite convincingly proved by the following reactions.

Bis-(triethylgermyl)-cadmium, when heated in an evacuated ampoule to 125—130°, decomposes with the formation of metallic cadmium and hexaethyldigermane. Their yields are 97.0 and 73.5%. Tetraethylgermane or gaseous products are not formed in this process, which indicates the absence of Cd—C_2H_5 groupings in the decomposing compound.

Bis-(triethylgermyl)-cadmium is vigorously oxidized by atmospheric oxygen. The reaction can be described by the equation

$$2(C_2H_5)_3GeCdGe(C_2H_5)_3 + O_2 \rightarrow 2(C_2H_5)_3GeOGe(C_2H_5)_3 + 2Cd.$$

The yields of bis-triethylgermanium oxide and cadmium are, respectively, 69.5 and 100.0%. As is known ([1]), the oxidation of bis-(triethylgermyl)-mercury proceeds in a similar manner.

On the other hand, the exothermic reactions of bis-(triethylgermyl)-cadmium and its mercury analogue with benzoyl peroxide differ noticeably from one another. The organogermanium-cadmium compound reacts with two moles of peroxide, forming triethylgermyl benzoate and cadmium dibenzoate, the yields of which are respectively 64.6 and 98.6%. For bis-(triethylgermyl)-mercury, reaction with an equimolar amount of peroxide is characteristic, as a result of which mercury is liberated in the free state ([1]).

In general, the compared bimetallic organic compounds differ considerably in chemical properties. Thus, for example, reactions of bis-(triethylgermyl)-cadmium with alkyl bromides proceed at a noticeable rate already at room temperature according to the equation

$$2RBr + (C_2H_5)_3GeCdGe(C_2H_5)_3 \rightarrow CdBr_2 + 2(C_2H_5)_3GeR,$$

$$R = C_2H_5 \text{ and } C_6H_5CH_2.$$

Under the same temperature conditions, bis-(triethylgermyl)-mercury reacts with alkyl bromides only under the action of light and by an entirely different scheme ([3]):

$$2RBr + (C_2H_5)_3GeHgGe(C_2H_5)_3 \xrightarrow{h\nu} R_2Hg + 2(C_2H_5)_3GeBr.$$

We also established that bis-(triethylgermyl)-cadmium is slowly decomposed by water with the liberation of metallic cadmium, bis-triethylgermanium oxide, and triethylgermane. The yields of these substances are respectively 100, 98.1, and 43.9%. Under ordinary conditions bis-(triethylgermyl)-mercury does not react with water even after contact for many days.

The exothermic reaction of bis-(triethylgermyl)-cadmium with 1,2-dibromoethane is completed in 2–3 min. Its products are cadmium bromide, ethylene, and triethylbromogermane. Their yields are 74.0, 73.1, and 85.9% of those calculated according to the equation

$$(C_2H_5)_3GeCdGe(C_2H_5)_3 + 2BrCH_2CH_2Br \rightarrow CdBr_2 + 2(C_2H_5)_3GeBr + 2C_2H_4.$$

Experimental Part

All reactions were carried out in evacuated sealed ampoules. Operations for preparing the starting mixtures and for isolating the readily oxidized bis-(triethylgermyl)-cadmium were performed in evacuated systems in special apparatus.

Bis-(triethylgermyl)-cadmium. 8.60 g of triethylgermane and 4.92 g of diethylcadmium are heated in ampoules for 3 h at 80–85°. 1080 ml (90.4%) of ethane and traces of metallic cadmium are liberated. The reaction mixture is kept for 5–6 h in an evacuated sealed apparatus for redistillation with gradual heating of the mixture to 80–85° and simultaneous cooling of the receiver for volatile components with liquid nitrogen. The yield of bis-(triethylgermyl)-cadmium is 9.04 g (78.6%). The non-distilling liquid, lemon-yellow in color, deposits cadmium on contact with air.

Thermal decomposition of bis-(triethylgermyl)-cadmium. 1.30 g of the substance is heated for 7 h to 125–130°. 0.32 g (97.0%) of cadmium is liberated. The decolorized reaction mixture is decanted from the cadmium and distilled. 0.71 g (73.5%) of hexaethyldigermane is obtained. B.p. 110–115° at 2 mm; n_D^{20} 1.4920, which agrees with the literature data (1).

Oxidation of bis-(triethylgermyl)-cadmium. An ampoule containing 1.20 g of the substance is opened and left overnight. 0.31 g (100%) of metallic cadmium is obtained. The decolorized reaction mixture is fractionated. 0.65 g (69.5%) of bis-triethylgermanium oxide is isolated. B.p. 130–132° at 20 mm; n_D^{20} 1.4600. Literature data (1): b.p. 130–132° at 20 mm; n_D^{20} 1.4612.

Reaction of bis-(triethylgermyl)-cadmium with benzoyl peroxide. A solution of 2.60 g of benzoyl peroxide in 15 ml of dry benzene is gradually added to 2.47 g of bis-(triethylgermyl)-cadmium. The exothermic reaction is accompanied by the separation of 2.00 g (98.6%) of cadmium dibenzoate. The product is titrated with NaOH solution using phenolphthalein.

$C_{12}H_{10}CdO_4$.	Found, %:	C_6H_5COO 68.13
	Calculated, %:	C_6H_5COO 68.35

Upon distillation of the reaction mixture, 2.08 g (64.6%) of benzoyloxytriethylgermane is isolated. B.p. 105–114° at 2 mm; n_D^{20} 1.5050. Literature data (1): b.p. 106–108° at 1.5 mm; n_D^{20} 1.5076.

$C_{13}H_{20}GeO_2$.	Found, %:	C_6H_5COO 43.70
	Calculated, %:	C_6H_5COO 43.11

Interaction of bis-(triethylgermyl)-cadmium with benzyl bromide. 7.66 g of benzyl bromide is frozen with liquid nitrogen and 2.72 g of bis-(triethylgermyl)-cadmium is added. On thawing, an exothermic reaction begins, ending in 3–5 min. 1.14 g (66.7%) of cadmium bromide is separated. Fractionation of the mixture gives 1.20 g (38.2%) of triethylbenzylgermane.

B.p. 95–105° at 2 mm; n_D^{20} 1.5165. Literature data ([5]): b.p. 78–81° at 1 mm; n_D^{20} 1.5178.

The interaction of 2.12 g of bis-(triethylgermyl)-cadmium and 2.95 g of ethyl bromide proceeds less vigorously (3 h at ~20°). The yields of cadmium bromide and tetraethylgermane are respectively 82.8 and 70.9%.

Reaction of bis-(triethylgermyl)-cadmium with water. A mixture of 2.20 g of bis-(triethylgermyl)-cadmium and 5.0 ml of water is shaken and left overnight. 0.57 g (100%) of cadmium is liberated. The organic layer is dried over $CaCl_2$ and fractionated. This gives 0.36 g (43.9%) of triethylgermane with b.p. 120–125° at 760 mm; n_D^{20} 1.4310, and 0.84 g (98.1%) of bis-triethylgermanium oxide. B.p. 88–90° at 2 mm; n_D^{20} 1.4605, which agrees with the literature data ([1]).

Received
14 V 1964

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