REACTIONS OF SELECTIVE CLEAVAGE OF Ge – Cd BONDS OF bis-(TRIETHYLGERMYL) CADMIUM*

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As is well known [1], biheteroorganic compounds of the series $(R_3E)_nM$, where E = Si, Ge, Sn; M = Zn, Cd, Hg, Tl, Sb, Bi, Se, Te; n = 2, 3, possess high reactivity. However, the mechanism of most of the investigated reactions remains in dispute, since the reaction conditions led to an uncontrollable cleavage of all the E–M bonds in the molecule.

We recently demonstrated that in the hydrolysis, alcoholysis, and acidolysis of bis(triphenylgermyl) cadmium, there is a step-by-step cleavage of the Ge–Cd bonds [2]. In this work we describe two types of reactions, in which the labile Ge–Cd bonds of bis(triethylgermyl) cadmium (I) are also cleaved selectively.

The interaction of compound (I) with acetic and benzoic acids or with phenol proceeds with heterolytic cleavage of only 1 Ge–Cd bond, if the reaction is conducted at 5-10° in a solution of toluene or hexane at a 1:1 mole ratio of the reagents.

$$\underset{\text{(I)}}{[(C_2H_5)_3Ge]_2Cd} + ROH \rightarrow \underset{\text{(II a, b, c)}}{(C_2H_5)_3GeCdOR} + (C_2H_5)_3GeH \qquad (1)$$

$$\text{a } R{=}CH_3CO;\ \text{b } R = C_6H_5CO;\ \text{c } R{=}C_6H_5$$

In the acidolysis of CH_3COOH, the yields of triethylgermane and acetyloxy(triethylgermyl) cadmium (IIa) are correspondingly equal to 89.5 and 81.2%. In the reaction with benzoic acid, triethylgermane (72.6%) and benzoyloxy(triethylgermyl) cadmium (IIb) (73.8%) are formed. The compounds (IIa, b) are crystalline, readily oxidized substances, thermally less stable than their $(C_6H_5)_3GeCdOR$ analogs [2]. Thus, the compound (IIa) already decomposes slowly at ~20°. In toluene solution at 100°, the decomposition ends in 2 h with the formation of cadmium (100%) and acetyloxytriethylgermane (52.7%).

The molecules of organocadmium compounds of the series RCd–OR' (R and R' are hydrocarbon radicals) form stable cyclic associates $(RCd{-}OR')_n$ with O → Cd coordination bonds [3]. Judging by the determination of the molecular weight (cryoscopy), compound (IIb) is monomeric in benzene solution, and, consequently, in this case the cadmium atom is less coordination saturated than in the associates $(RCd{-}OR')_n$. This may explain the fact that in the interaction of bis(triethylgermyl) cadmium with two moles of CH_3COOH in hexane medium at 5-10°, when cleavage of both Ge–Cd bonds might have been expected, the compound (IIa) intermediately formed reacts with CH_3COOH, giving a complex compound (III)

$$[(C_2H_5)_3Ge]_2Cd + 2CH_3COOH \rightarrow (C_2H_5)_3GeH + (C_2H_5)_3GeCdOCOCH_3 \cdot CH_3COOH \text{ (III)} \qquad (2)$$

Stable complexes with a 1:1 composition are also formed in the interaction of compounds (IIa, b, c) with pyridine or dioxane. In particular, compound (IIc) can be isolated in the individual state only in the form of the complex $(C_2H_5)_3GeCdOC_6H_5 \cdot C_5H_5N$ (IV). In the case when reaction (1) between phenol and compound (I) is conducted in the absence of pyridine, only decomposition products of compound (IIc) are formed – metallic cadmium and phenoxytriethylgermane.

The reactions of protolytic cleavage discussed evidently proceed through a four-center transition state (V) according to an S_Ei-mechanism. The transition state is characterized by simultaneous nucleophilic attack on the cadmium atom and electrophilic attact on the germanium atom (Scheme 1).

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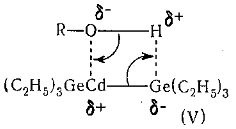
(V)

Scheme 1

It is known [1] that biheteroorganic compounds of the series $(R_3E)_nM$ react under mild conditions with dialkylperoxides with cleavage of all the E–M bonds. We have shown that in the interaction of bis(triethylgermyl) cadmium and bis(triphenylgermyl) cadmium with equimolar amounts of benzoyl peroxide (BP) in toluene solution, cleavage of the Ge– Cd bonds proceeds selectively

$$(R_3Ge)_2Cd + (C_6H_5COO)_2 \rightarrow \underset{\text{(IIb), (VI)}}{R_3GeCdOCOC_6H_5} + R_3GeOCOC_6H_5 \qquad (3)$$
$$\text{(IIb) } R = C_2H_5;\ \text{(VI) } R = C_6H_5$$

Compound (VI) was isolated in the form of the complex $(C_6H_5)_3GeCdOCOC_6H_5 \cdot 2C_5H_5N$ (VII). The yields of the compounds (IIb) and (VII) reached 60%. The interaction of compound (VI) produced according to the method of [2], with still another mole of BP proceeds under somewhat more rigorous conditions with the formation of cadmium benzoate (93.4%) and benzoyloxytriphenylgermane (92.6%)

$$(C_6H_5)_3GeCdOCOC_6H_5 + (C_6H_5COO)_2 \rightarrow Cd\ (OCOC_6H_5)_2 + (C_6H_5)_3GeOCOC_6H_5 \qquad (4)$$

This observation, as well as the selective cleavage of the Ge–Cd bonds in the reactions described by Eqs. (1)-(3), show that the Ge– Cd bonds in compounds (IIa, b) and (VI) are stronger in comparison with the initial germylcadmium derivatives. In view of this, let us note that mercury analogs of the type of R_3GeHgX, where X is an electron attracting substituent (Cl, Br, I, CN, $OCOCH_3$, $OCOC_6H_5$, etc.), are extremely unstable and decompose at the moment of formation [4-6].

EXPERIMENTAL METHOD

All the reactions were conducted in evacuated sealed instruments. The reagents and solvents were freed of atmospheric oxygen before use. The boiling points of germylcadmium compounds were determined in a sealed evacuated capillary.

Reaction of bis(Triethylgermyl) Cadmium (I) with Acetic Acid. Mole Ratio 1 : 1. To a solution of 4.95 g of compound (I) in 15 ml of hexane at 5-10° we gradually added a solution of 0.68 g glacial CH_3COOH in 15 ml of hexane. The mixture was kept for 1 h at ~20° and evaporated under vacuum. The residue was extracted with chilled hexane and dried under vacuum. We obtained 3.08 g (81.2%) acetyloxy(triethylgermyl) cadmium (IIa) with $t_{decomp.}$ ~55°. Found: Cd 33.60%. $C_8H_{18}CdGeO_2$. Calculated: Cd 33.94%.

Fractionation of the hexane extract yielded 1.65 g (89.5%) triethyl germane; bp 122-124°; n_D^{20} 1.4360. According to the data of [7]: bp 124° (760 mm); n_D^{20} 1.4382.

Synthesis of the Complex $(C_2H_5)_3GeCdOCOCH_3 \cdot C_5H_5N$ (VIII). Under the conditions of the preceding experiment, but with an addition of 2 ml of pyridine to the reaction mixture, from 3.13 g of compound (I) and 0.42 g CH_3COOH in 35 ml of toluene we obtained 0.98 g (85.0%) triethylgermane and 2.30 g (72.2%) of the complex (VIII); colorless crystalline substance with mp 62-64°. Found: Cd 27.05%. $C_{13}H_{23}CdGeNO_2$. Calculated: Cd 27.39%.

Mole Ratio 1 : 2. To a solution of 3.90 g of compound (I) in 15 ml of hexane at 5-10° we added a solution of 1.08 g CH_3COOH in 15 ml of hexane. Part of the solvent was distilled off under vacuum, and the residue left for 12 h at –5 to 0°. The crystalline precipitate was extracted with hexane and dried under vacuum. We obtained 2.83 g (80.2%) of the complex $(C_2H_5)_3GeCdOCOCH_3 \cdot CH_3COOH$ (III); colorless crystalline substance with $p_{decomp.}$ ~65°, poorly soluble in hexane and toluene. Found: Cd 28.85% $C_{10}H_{22}CdGeO_4$. Calculated: Cd 28.73%.

Thermal Decomposition of Compounds (IIa) and (III). A solution of 1.69 g of compound (IIa) in 15 ml of toluene was heated for 2 h to 100°. The organic layer was decanted from the precipitate and fractionated. We obtained 0.59 g (52.7%) of acetyloxytriethylgermane with bp 75-77° (20 mm); n_D^{20} 1.4453. According to the data of [8]: bp 99-100° (60 mm); n_D^{20} 1.4430. The precipitate was extracted with acetone, dried under vacuum, and dissolved in nitric acid. We determined 0.58 g (100%) cadmium by titration with Trilon B.

Analogously, by heating a mixture of 2.83 g of the complex (III) and 15 ml of toluene (5 h at 100°) we obtained 0.85 g (53.8%) acetyloxytriethylgermane with bp 75-77° (20 mm); n_D^{20} 1.4410; 0.81 g (99.6%) cadmium; and 0.39 g (92%) CH_3COOH, identified by the method of gas–liquid chromatography.

Reaction of Compound (I) with Benzoic acid. To a solution of 4.20 g of compound (I) in 20 ml of toluene we added a solution of 1.16 g benzoic acid in 10 ml of toluene at 5-10°. The solvent was distilled off under vacuum. The residue was left overnight at the temperature –5 to 0°. The crystalline precipitate formed was extracted with chilled hexane and dried under vacuum. We obtained 2.82 g (73.8%) benzoyloxy · (triethylgermyl) cadmium (IIb) with mp 86° (with decomp.). Found: Cd 28.00%; mol. wt. 414. $C_{13}H_{20}Cd \cdot GeO_2$. Calculated: Cd 28.58%; mol. wt. 393. We isolated 1.19 g (76.2%) triethylgermane with bp 122-124°; n_D^{20} 1.4370.

Interaction of Compound (I) with Benzoyl Peroxide. Mole Ratio 1 : 1. To a solution of 4.00 g of compound (I) in 20 ml of toluene, we added a solution of 2.24 g benzoyl peroxide in 15 ml of toluene at 5-10°. Most of the toluene was distilled off under vacuum, and the residue left overnight at –5 to 0°. The crystalline residue was extracted with hexane and dried under vacuum. We obtained 1.70 g (46.4%) of compound (IIb) with mp 85° (with decomp.). Found: Cd 28.45%. $C_{13}H_{20}CdGeO_2$. Calculated: Cd 28.58%.

To the hexane extract we added 10 ml of dioxane and left at ~20° for 12 h. An additional 0.82 g (18.4%) of compound (IIb) crystallized from the solution in the form of the dioxanate $(C_2H_5)_3GeCdOCOC_6H_5 \cdot C_4H_8O_2$, mp 97° (with decomp.). Found: C 42.60; H 5.64%. $C_{17}H_{28}CdGeO_4$. Calculated: C 42.42; H 5.86%.

In fractionation of the mother liquor we obtained 2.00 g (77.8%) benzoyloxytriethylgermane with bp 106-107° (1.5 mm); n_D^{20} 1.5060. According to the data of [9]: bp 106-108° (1.5 mm); n_D^{20} 1.5076.

Reaction of bis(Triphenylgermyl) Cadmium with Benzoyl Peroxide. Mole Ratio 1 : 1. To a solution of 3.10 g bis(triphenylgermyl) cadmium in 15 ml of toluene at 5-10° we gradually added a solution of 1.04 g BP in 10 ml of toluene. The mixture was left at ~20° overnight, and 2 ml of pyridine was added. Readily volatile products were distilled off under vacuum, and the residue was extracted with hexane and dried. We obtained 1.86 g (62.8%) of the complex $(C_6H_5)_3GeCdOCOC_6H_5 \cdot 2C_5H_5N$ (VII); colorless crystalline substance with mp 135°. Found: C 60.05; H 4.26; Cd 16.10%. $C_{35}H_{30}CdGeN_2O_2$. Calculated: C 60.43; H 4.35; Cd 16.16%.

The hexane extract was evaporated, the residue recrystallized from a mixture of toluene and hexane. We obtained 1.02 g (55.7%) of benzoyloxytriphenylgermane with bp 108°. A mixed sample with the pure substance gave no depression of the melting point.

Reaction of Benzoyloxy(triphenylgermyl) Cadmium (VI) with Benzoyl Peroxide. To a solution of 2.20 g of compound (VI) [2] in 20 ml of toluene we added a solution of 1.00 g BP in 20 ml of toluene and left the mixture overnight. We isolated 1.36 g (93.4%) cadmium benzoate. Found: Cd 31.18%. $C_{14}H_{10}CdO_4$. Calculated: Cd 31.69%. From the toluene solution 1.61 g (92.6%) benzoyloxytriphenylgermane with mp 110° was isolated in the usual way.

Reaction of Compound (I) with Phenol. Mole Ratio 1 : 1. A mixture of 3.30 g of compound (I), 0.77 g phenol, 2 ml of pyridine, and 20 ml of toluene was heated to 100° (1 h). Readily volatile products were distilled off under vacuum. A crystalline product was extracted with chilled hexane and dried under vacuum. We obtained 2.99 g (88.5%) of the complex $(C_2H_5)_3GeCdOC_6H_5 \cdot C_5H_5N$ (IV); colorless crystals with bp 80°, readily soluble in toluene and hexane. Found: C 46.00; H 5.70; Cd 25.50%. $C_{17}H_{25}CdGeNO$. Calculated: C 45.95; H 5.67; Cd 25.29%. From the hexane extract 0.78 extract 0.78 g (64.0%) triethylgermane was isolated in the usual way.

A mixture of 4.95 g of compound (I), 1.06 g phenol, and 30 ml of toluene was left at ~20° for four days. We isolated 1.27 g (98.4%) cadmium. The organic layer was fractionated. We obtained 1.37 g (75.0%) triethylgermane with bp 122-124°; n_D^{20} 1.4369 and 2.35 g (81.7%) phenoxytriethylgermane with bp 138-140° (18 mm); n_D^{20} 1.5080. According to the data of [10]: bp 140° (18 mm); n_D^{20} 1.5102.

CONCLUSIONS

1. In the reaction of phenol, acetic and benzoic acids with an equimolar amount of bis(triethylgermyl) cadmium, there is a selective heterolysis of the Ge–Cd–Ge group, and phenoxy- or acyloxy(triethylgermyl) cadmium compounds are formed, respectively.

2. The reaction of benzoyl peroxide with bis(triethylgermyl)- and bis(triphenylgermyl) cadmium leads to selective cleavage of the heteroelement–heteroelement bonds.

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