REACTION OF HETEROORGANIC CHALCOGENIDES

WITH SOME MERCURY DERIVATIVES

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It is known that bis(trialkylsilyl) sulfides, $(R_3Si)_2S$, react smoothly with HgX_2 compounds (X=Cl [1], CH₂COR [2], C(N₂)COOC₂H₅ [3], COOCH₃ [4], COON (C₂H₅)₂ [5]), with the formation of mercury sulfide and derivatives of the R_3SiX type.

It was shown by us that bis(triethylsilyl) selenide, bis(triethylsilyl) telluride and their germanium analogs react with mercury salts by the same scheme.

$$[(C_2H_5)_3M]_2E + HgX_2 \rightarrow (C_2H_5)_3MX + HgE$$

$$M = \text{Si, Ge; } E = \text{Se, Te; } X = \text{Cl, CN}$$
(1)

The reaction of bis(triethylsilyl) selenide with ethylmercury chloride proceeds in a more complicated manner. Here the products are triethylchlorosilane, bis(triethylsilyl) selenide, the previously unknown bis(ethylmercury) selenide (I), diethylmercury and mercury selenide. Taking into account the general character of the processes, described by Eq. (1), and the presence of Hg—Cl in the ethylmercury chloride fragment, it is possible to postulate the following initial step of the reaction:

$$[(C_2H_5)_3Si]_2Se + C_2H_5HgCl \rightarrow (C_2H_5)_3SiCl + (C_2H_5)_3SiSeHgC_2H_5$$
(II) (II) (2)

As is known [6], selenides of the R_3M -Se-M' R_3 series (R = alkyl; M and M' = Ge, Sn, Pb) are symmetrized with exceeding ease. The amount of the symmetrization products $[(C_2H_5)_3Si]_2Se$ (II) and $(C_2H_5Hg)_2Se$ (I) in the reaction mixture can be explained in this way. Mercury selenide and diethylmercury are probably formed via a partial decomposition of compound (I).

Previously we have shown that the reaction of triethylsilylhydroselenide, $(C_2H_5)_3SiSeH$, with an equimolar amount of triethylaluminum proceeds with a selective heterolysis of the C-Al bond, leading to the formation of ethane and $(C_2H_5)_3SiSeAl(C_2H_5)_2$ [7].

An attempt to obtain (II) by the reaction of one mole of $(C_2H_5)_3$ SiSeH with diethylmercury proved unsuccessful. Together with ethane, a complex mixture of products was obtained. In contrast, the selective heterolytic cleavage of bis(triethylgermyl)mercury by either triethylsilylhydroselenide or triethylsilylhydrotelluride in hexane medium proceeds under very mild conditions (respectively at -20 and -78° in 2-3 min), with the formation of triethylgermyl(triethylsilylseleno)mercury (IIIa) and its tellurium-containing analog (IIIb).

$$(C_{2}H_{5})_{3}SiXH + [(C_{2}H_{5})_{3}Ge]_{2}Hg \rightarrow (C_{2}H_{5})_{3}GeH + (C_{2}H_{5})_{3}SiXHgGe(C_{2}H_{5})_{3}$$

$$X = Se(a); Te(b) \qquad (III) \qquad (3)$$

If the reaction between either triethylsilylhydroselenide or the telluride analog and bis(triethylgermyl)mercury in hexane solution is run at a 2:1 ratio of the reactants, there is respectively formed, together with triethylgermane, either bis(triethylseleno)mercury (IVa) or bis(triethylsilyltelluro)mercury (IVb), but the substitution of two (C_2H_5)₃Ge groups proceeds under more drastic conditions (30 min at 50°).

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		Yield.					ound.	0%					Calc	ulated,	9%		
DN	Compound	20	Mp, C	υ	н	Ge	Нg	Se	Si	Te	υ	н	Ge	Hg	Se	Si	Te
I	$(C_2H_5Hg)_2Se$	35,4	105-108(de-	8,96	2,04	1	73,66	13,05	[I	8,93	1,87		74,53	14,67		l
IIIa	(C2H3)3SiSeHgGe (C2H5)3	13,0	36 (decompn.)	1		1	36,08	14,15	1			1		36,22	14,25		1
III	(C2H5)3SiTeHgGe (C2H5)3	33,5	72(decompn)	1	1	12,05	33,68	1	4,65	21,50			12,03	33,35]	4,65	21,15
IV a	[[(C2H5)3SiSe]2Hg	47,4	81 (decompn)	I	l		34,88	26,30			1.	1	1	34,05	26,81	!	1
lVb	[(C2H5)3SiTe]2Hg	34,0	104 (decompn)	ŀ	1		29,58	1	9,07	37,67				29,20	1	8,18	37,18
Ν	(C ₂ H ₅) ₃ SiSHgGe (C ₂ H ₆) ₃	60,0	-15 to -13	1	l	13,85	38,50	1	5,30		I	1	14,30	39,50		5,53	I
VI a	(C ₂ H ₅) ₃ SiSGe (C ₂ H ₅) ₃	68, 1	*	47,19	9,91	23,16	I	1	8,96		⁴ 6,93	9,85	23,64	1	1	9,15	l
dΙV	$(C_2H_5)_3SiSeGe (C_2H_5)_3$	72,7	+	40,78	8,37	20,33	1	23,01	7,87		40,71	8,54	20,51		22,30	7,93	1
VI c	(C ₂ H ₅) ₃ SiTeGe (C ₂ H ₅) ₈	90,0	++		I	18,55	1		6,90	31,03			18,03			3,97	31,69
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TABLE 1. Properties and Analysis of Obtained Compounds

^{*}Bp 98-99° (3 mm), n_D^{20} 1, 5028 Found: S 9, 84%. Calculated: S 10, 44%, $\ddagger Bp$ 109-110° (3 mm), n_D^{20} 1, 5177. ‡ Bp 118-119° (3 mm), n_D^{20} 1, 5548.

$2(C_{2}H_{5})_{3}SiXH + [(C_{2}H_{5})_{3}Ge]_{2}Hg \rightarrow 2 (C_{2}H_{5})_{3}GeH + [(C_{2}H_{5})_{3}SiX]_{2}Hg$

$$X = Se(a); Te(b)$$

Triethylsilylhydrosulfide, $(C_2H_5)_3SiSH$, does not react with bis(triethylgermyl)mercury under comparable conditions, while at 70° despite an excess of the hydrosulfide, the formation of the monosubstituted product, namely triethylgermyl(triethylsilylthio)mercury (V), and triethylgermane is observed. Compounds of the series $(C_2H_5)_3SiXHgGe(C_2H_5)_3$ (X=S, Se, Te) can be isolated from the reaction mixture in the crystalline state by low-temperature crystallization. When stored they are easily decomposed at ~20° according to the scheme:

$$(C_{2}H_{5})_{3}SiXHgGe(C_{2}H_{5})_{3} \rightarrow Hg + (C_{2}H_{5})_{3}SiXGe(C_{2}H_{5})_{3}$$
(VI)
$$X=S (a); Se (b); Te (c)$$
(5)

(4)

The symmetrical products, $[(C_2H_5)_3SiX]_2Hg$, are colorless crystalline compounds. They are difficultly soluble in hexane and are thermally stable; in solutions they fail to decompose completely even on long heating (7 h at 130°), in which connection their decomposition products are mercury selenide and compounds of the type $[(C_2H_5)_3Si]_2X$.

EXPERIMENTAL SECTION

<u>Reaction of bis(Triethylgermyl) Telluride with Mercuric Chloride</u>. To 2.27 g of $HgCl_2$ in 10 ml of THF at 20°C was added 3.74 g of bis(triethylgermyl) telluride. Here a slight warming up of the mixture and the separation of the HgTe precipitate were observed. The mixture was heated at 50° for 1 h; the precipitate was filtered (2.70 g, 98.2%). Fractional distillation gave 1.94 g (60.1%) of $(C_2H_5)_3$ GeCl with bp175° and n_D^{20} 1.4620. From [8]: bp175.9°; n_D^{20} 1.4645.

The reactions of $[(C_2H_5)_3Si]_2Se$ and $[(C_2H_5)_3Ge]_2Se$ with mercuric chloride proceeded in a similar manner.

Under comparable conditions, from 0.99 g of Hg(CN)₂ and 1.20 g of bis(triethylsilyl) selenide in 10 ml of THF was obtained 1.05 g (97.5%) of HgSe and 0.61 g (54.7%) of triethylcyanosilane with bp 94° (40 mm); n_D^{20} 1.4278. The compound was identified by GLC.

Reaction of bis(Triethylsilyl) Selenide with Ethylmercury Chloride. To 1.11 g of C_2H_5 HgCl in 10 ml of toluene was added 1.31 g of bis(triethylsilylgermyl) selenide. The mixture was heated at 80° for 3 h. The organic layer was decanted from the HgSe precipitate (0.15 g, 26.8%) and cooled to -70° (5 h). The obtained colorless crystals of (I) were washed with chilled toluene (see Table 1). In the mother liquor by GLC were detected 0.51 g (80.5%) of triethylchlorosilane, 0.61 g (94.0%) of bis(triethylsilyl) selenide, and 0.09 g (16.7%) of diethylmercury.

Reaction of Triethylsilylhydroselenide with bis (Triethylgermyl)mercury. a) Using an equimolar ratio. To 3.40 g of bis (triethylgermyl)mercury in 8 ml of hexane at -20° was added 1.27 g of $(C_2H_5)_3$ SiSeH. After 1-3 min the characteristic yellow color of the germylmercury compound disappeared. The mixture was cooled to -78° (6 h). The obtained colorless crystals of (III) were recrystallized three times from hexane at -78° (0.47 g). In the mother liquor by GLC was detected 0.84 g (80.7%) of triethylgermane.

b) Using a 2:1 ratio. A mixture of 1.15 g of $(C_2H_5)_3$ SiSeH, 1.51 g of $[(C_2H_5)_3Ge]_2$ Hg and 7 ml of hexane, prepared as indicated above was heated at 50° for 30 min, after which it was cooled at 0° for 6 h. We isolated 0.81 g of (IVa). By GLC was detected 0.71 g (76.3%) of triethylgermane.

Compound (IVb) was obtained in a similar manner.

<u>Triethylgermyl(triethylsilylthio)mercury (V)</u>. A mixture of 1.24 g of $(C_2H_5)_3SiSH$, 2.21 g of bis(triethylgermyl)mercury and 6 ml of hexane (ratio of the reactants = 2:1) was heated at 70° for 30 min, after which it was cooled to ~ -90° for 5 h. The obtained colorless crystals were recrystallized twice from hexane at -90°. We obtained 1.21 g of (V).

Reaction of Triethylsilylhydrotelluride with bis(Triethylgermyl)mercury. To 2.26 g of bis(triethylgermyl)mercury in 17 ml of pentane (equimolar ratio) at -78° was added 1.13 g of (C₂H₅)₃SiTeH. The obtained mixture was kept at the same temperature for 6 h. The obtained colorless crystals of (IIIb) were washed twice with pentane at $\sim -70^{\circ}$ (0.88 g). In the mother liquor by GLC was found 0.47 g (68%) of triethylgermane.

<u>Thermal Decomposition of Triethylgermyl(triethylsilyltelluro)mercury (IIIb)</u>. Compound (IIIb), obtained as described above from 0.89 g of $(C_2H_5)_3$ SiTeH and 1.98 g of bis(triethylgermyl)mercury in 4 ml of hexane, without isolation from the reaction mixture, was allowed to stand at room temperature overnight. The organic layer was decanted from the mercury (0.71 g, 97.3%) and fractionally distilled. We isolated 1.32 g of (VIc). In the light fractions by GLC was detected 0.41 g (69%) of triethylgermane, which was formed according to reaction (3). The same composition of the products was obtained when (IIIb) was decomposed in the absence of a solvent.

Compounds (VIa) and (VIb) were obtained in a similar manner (see Table 1).

Thermal Decomposition of bis(Triethylsilylseleno)mercury (IVa). Compound (IVa) (obtained, as described above, by heating a mixture of 0.83 g of $(C_2H_5)_3$ SiSeH and 1.15 g of $[(C_2H_5)_3Ge]_2$ Hg in 2 ml of toluene, 50°, 30 min), without isolation from the reaction mixture, was heated at 130° (7 h). The obtained precipitate of HgSe (0.52 g, 88%) was separated by decantation. By GLC was found 0.63 g (93.1%) of triethylgermane, which was formed according to reaction (4), and 0.63 g (95.5%) of $[(C_2H_5)_3Si]_2$ Se.

The decomposition of (IVb) was run in a similar manner.

CONCLUSIONS

1. Bis(triethylsilyl) selenide, bis(triethylsilyl) telluride, and their germanium analogs, react with mercury salts, HgX_2 (X = Cl,CN), forming the mercury chalcogenide and the compound $(C_2H_5)_3MX$ (M = Si, Ge).

2. The reaction of $[(C_2H_5)_3Si]_2Se$ with ethylmercury chloride gives triethylchlorosilane and bis(ethylmercury) selenide.

3. By reacting hydrochalcogenides of the series $(C_2H_5)_3SiXH$ (X=S,Se, Te) with bis(triethylgermyl)mercury, using either a 1:1 or a 1:2 ratio, were respectively synthesized derivatives of the type $(C_2H_5)_3Si-XHgGe(C_2H_5)_3$ and $[(C_2H_5)_3SiX]_2Hg$.

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