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## Preliminary communication

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# Syntheses of chalcogen containing silyl- and germyl-mercury compounds

E.N. GLADYSHEV, N.S. VYAZANKIN, V.S. ANDREEVICHEV, A.A. KLIMOV and
G.A. RAZUVAEV

*Institute of Chemistry, U.S.S.R. Academy of Sciences, Gorky (U.S.S.R.)*

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Recently, germylmercury compounds with a novel Si—X—Hg—Ge skeleton (X = S, Se, Te) have been prepared by the reaction of triethylsilanethiol and its analogues with an equimolecular amount of bis(triethylgermyl)mercury under controlled conditions[1]. We wish to report in this communication the synthesis of similar compounds containing Si—X—Hg—Si and Ge—X—Hg—Ge groupings (X = S, Se) by the reaction of sulphur and selenium with disilyl- and digermyl-mercury compounds (1/1 molar ratio) in pentane, hexane or in the absence of a solvent.

$$(R_3M)_2Hg + 1/8\, X_8 \rightarrow R_3M{-}X{-}Hg{-}MR_3 \qquad (1)$$

$$(M = Si, Ge;\ R = Et \text{ or } i\text{-}Pr;\ X = S, Se)$$

Details of experiments are given in Table 1. Under similar conditions tellurium reacts with bis(triethylgermyl)mercury in pentane yielding mercury (88% yield), HgTe (15%), bis(triethylgermyl) telluride (58%) and hexaethyldigermane (39%). Reaction (1) is believed to proceed through the intermediate formation of $R_3M{-}X{-}(X)_6{-}XHgMR_3$. Subsequent degradation of the chalcogen chain occurs via reaction of the intermediate product with the initial mercury compound.

This suggestion is in accord with the reactions of bis(triethylsilyl)- and bis(triethylgermyl)-mercury with diethyl disulphide, in the course of which mercury (92—96% yields) and triethyl(ethylthio)silane (or -germane) in 80—90% yields are formed. These latter reactions were carried out in the absence of solvent at 100° (10h) with the reactants in a mole ratio of 1/1. The formation of the products observed in these reactions may be explained by the mechanism given in Eqn. (2a,b)

$$\begin{tikzcd}
(Et_3M)_2Hg + EtSSEt \arrow[r, "a"] & Et_3MSEt + Et_3MHgSEt \arrow[d, "b"] \\
(M = Si, Ge) & Hg + Et_3MSEt
\end{tikzcd} \qquad (2)$$

In the compound $Et_3MHgSEt$ (M = Si, Ge) mercury is bonded with an electron-withdrawing $C_2H_5S$ group. Since similar silyl- and germyl-mercury compounds, $Et_3M{-}Hg{-}X$, (X = electronegative substituent) are unstable[2-4] and decompose to mercury and $R_3MX$, it is not unreasonable to suppose that $Et_3MHgSEt$ would decompose to $Et_3MSEt$ in accord with Eqn. (2b).

The compounds listed in Table 1 were isolated from the reaction mixture in the crystalline state after low-temperature (–75°) crystallization. Cryoscopic molecular weight measurements showed that $i\text{-}Pr_3GeXHgGe\text{-}i\text{-}Pr_3$, where X = S, Se, and $Et_3SiSeHgSiEt_3$ are monomeric in benzene solution. In contrast, bis(triethylgermyl)-cadmium has been found to react with sulphur and selenium to give the bridged dimeric entities $[Et_3GeSCdGeEt_3]_2$ and $[Et_3GeSeCdGeEt_3]_2$, respectively[5]. All these compounds when dissolved in hexane underwent a very slow decomposition at room temperature, the process being catalysed by triethylamine and ethyl bromide.

The structures of the compounds listed in Table 1 were confirmed by ultraviolet photolysis *viz.*,

$$R_3M{-}X{-}HgMR_3 \xrightarrow[\text{pentane}]{h\nu} R_3M{-}X{-}MR_3 + Hg \qquad (3)$$

Thus, photolysis of triisopropylgermyl(triisopropylgermylthio)mercury, and its selenium containing analogue, led to the formation of the previously unreported compounds, bis(triisopropylgermyl) sulphide (57% yield), m.p. 32.5–33.5°, and bis(triisopropylgermyl) selenide (63%), m.p. 27–27.5°, respectively.

TABLE 1

COMPOUNDS PREPARED BY THE INSERTION OF CHALCOGEN INTO Si–Hg AND Ge–Hg BONDS

| Compound [a] | Reaction solvent | Temp. (°C) | Time (h) | M.p. (°C) | Yield (%) |
|---|---|---|---|---|---|
| $(i\text{-}C_3H_7)_3GeSHgGe(i\text{-}C_3H_7)_3$ [b] | hexane [c] | 20 | 15 | 38.5 | 74.5 |
| $(i\text{-}C_3H_7)_3GeSeHgGe(i\text{-}C_3H_7)_3$ [b] | hexane | 20 | 17 | 42.5–43.5 | 90.9 |
| $(C_2H_5)_3GeSHgGe(C_2H_5)_3$ | pentane | 20 | 4 | –8 to –9 | 68.1 |
| $(C_2H_5)_3SiSHgSi(C_2H_5)_3$ | pentane | 20 | 4 | –44 | 54.7 |
| $(C_2H_5)_3GeSeHgGe(C_2H_5)_3$ | pentane | 20 | 10 | 55 | 64.9 |
| $(C_2H_5)_3SiSeHgSi(C_2H_5)_3$ [b] | pentane | 20 | 10 | 26.5 | 73.0 |
| $(C_2H_5)_3SiSHgGe(C_2H_5)_3$ | pentane | 20 | 10 | –15 | 69.0 |

[a] All compounds were characterized by microanalysis. [b] Compound monomeric in benzene solution (the cryoscopic molecular weight measurement). [c] In the absence of solvent the product yielded in 85%.

It was also shown that triethylsilyl(triethylsilylthio)mercury reacts with lithium in hexane at 20° for 2 days to give mercury (92%), HgS (traces) and a mixture of $Et_3SiLi$ and $Et_3SiSLi$. The formation of these lithium derivatives was confirmed through coupling reactions involving chlorodimethylsilane which afforded $Et_3SiSi(H)Me_2$, b.p. 56–58°/10mm; $n_D^{20}$ 1.4589, and $Et_3SiSSi(H)Me_2$, b.p. 87–89°/10mm; $n_D^{20}$ 1.4743, in yields of 55 and 60% respectively. In an attempted duplicate reaction, lithium was added to a solution of i-$Pr_3GeSHgGe$-i-$Pr_3$ in hexane (or benzene), but even after heating for 75 hours at 40° no reaction occurred. However, when i-$Pr_3GeSHgGe$-i-$Pr_3$ was allowed to react with lithium in tetrahydrofuran (46 hours at 40°), free mercury (92%) and a mixture of i-$Pr_3GeLi$ and i-$Pr_3GeSLi$ were formed. Treatment of the latter two species (after evaporation of THF under vacuum) with ethyl bromide in hexane solution at 75° for 9 hours gave i-$Pr_3GeSEt$ (71% yield), b.p. 130–132°/20mm; $n_D^{20}$ 1.4991, and hexaisopropyldigermane (60%), m.p. (mixed m.p.) 233–236°.

Bis(triisopropylgermyl)mercury is also less reactive than its ethyl analogue. In this case, the exchange reaction with metallic lithium in benzene was complete only after treatment of the reaction mixture at 40° for 3 days (*cf.* ref.6).

$$(\text{i-}Pr_3Ge)_2Hg + 2Li \rightarrow Hg + 2\ \text{i-}Pr_3GeLi \qquad (4)$$

Triisopropylgermyllithium was obtained in 83% yield from this exchange process. The reaction of i-$Pr_3GeLi$ with ethylene in benzene at 40° for 34 hours gave, after hydrolysis, ethyltriisopropylgermane in 54% yield, b.p. 99–100°/20mm; $n_D^{20}$ 1.4640.

All the above reactions were carried out in carefully evacuated, sealed ampoules.

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