

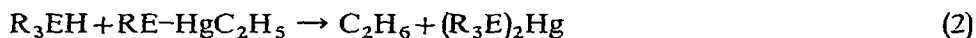
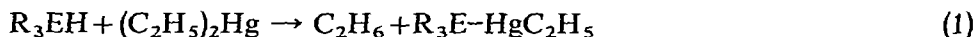
NOTE

SYNTHESIS OF ORGANOMETALLIC COMPOUNDS WITH Si-Hg-C AND Ge-Hg-C GROUPINGS

N. S. VYAZANKIN, E. N. GLADYSHEV, E. A. ARKHANGEL'SKAYA AND G. A. RAZUVAEV
Polymer Stabilization Laboratory, U.S.S.R. Academy of Sciences, Gorky (U.S.S.R.)

(Received February 6th, 1969)

It has previously been reported from this laboratory that silicon and germanium hydrides react with diethylmercury to form organometallic compounds with Si-Hg-Si and Ge-Hg-Ge groupings¹.



(E = Si, Ge; R = alkyl or aryl)

For example, this method has recently been used to prepare bis[tris(triethylgermyl)silyl]mercury, $\{[(C_2H_5)_3Ge]_3Si\}_2Hg$, and related compounds². Apparently, the replacement of the ethyl groups in diethylmercury occurs stepwise and consequently, unsymmetrical compounds with C-Hg-Si and C-Hg-Ge linkages are sometimes formed, e.g., ethyl(triethylsilyl)mercury³, ethyl(triethylgermyl)mercury⁴, and ethyl(pentaethyldisilanyl)mercury⁵.

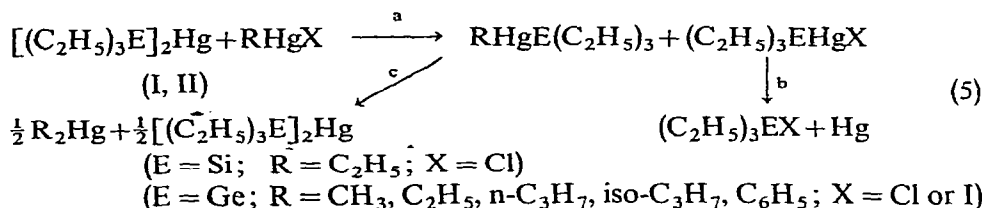
The present communication reports on the ready conversion on treatment with organomercuric halides of bis(triethylsilyl)mercury (I) and bis(triethylgermyl)mercury (II) into the corresponding derivatives having the C-Hg-Si and C-Hg-Ge bond system. This new method of preparation of such compounds has developed from the following observations: (i) ordinary organomercury compounds of type R_2Hg (R = alkyl or aryl) react with mercury(II) halides as follows⁶:



(ii) Seyferth and coworkers⁷ showed that bis(trimethylsilyl)mercury reacts with mercury(II) chloride exothermically to give chlorotrimethylsilane and metallic mercury. These compounds are produced by decomposition of an intermediate, $(CH_3)_3SiHgCl$, which is formed from the trimethylsilyl-chlorine exchange reaction of type (3) where $R = (CH_3)_3Si$ and $X = Cl$; (iii) when an ordinary mercury(II) derivative, R_2Hg , is treated with an organomercuric halide, equilibrium (4) takes place⁶.



We have found that a similar type of reaction between (I) or (II) and organomercuric halides proceeds according to the following scheme:



When these reactants were mixed at about 20° in the absence of a solvent, an uncontrollable, exothermic reaction commenced.

The reactions were carried out in the absence of solvent at -40° in evacuated ampoules with the reactants in a mole ratio, 1:1. All the reactions yielded unsymmetrical compounds of type, RHgE(C₂H₅)₃ (yields, 53–85%) together with metallic mercury and compounds (C₂H₅)₃EX. It was found, in all cases, in agreement with eqns. (5a) and (5b), that the yield of mercury is about 100%. The yield of compounds (C₂H₅)₃EX is also high (55–98%). Some R₂Hg and [(C₂H₅)₃E]₂Hg compounds were also present.

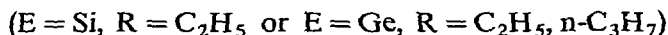
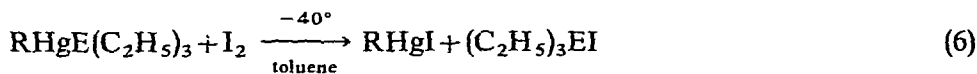
It is immediately evident that: (a) the mercury-for-mercury exchange reaction (5a), in contrast to reaction (4), is irreversible; (b) reaction (5a) proceeds with formation of (C₂H₅)₃EHgX as the transient intermediate; this is quantitatively consumed in the subsequent decomposition reaction (5b) to form metallic mercury and a compound of type (C₂H₅)₃EX; (c) the formation of R₂Hg and [(C₂H₅)₃E]₂Hg compounds indicates that the exchange reaction (5a) is accompanied by a disproportionation reaction (5c).

Thus, under the conditions described above, (I) reacts with ethylmercuric chloride giving ethyl(triethylsilyl)mercury in 84.7% yield, b.p. 80–85°/1.0 mm. (Found: Hg, 58.87. C₈H₂₀HgSi calcd.: Hg, 58.16%). Other reaction products isolated were mercury, chlorotriethylsilane, diethylmercury, and (I). Their yields, based on reactions (5a,b) and (5a,c), were 100, 90.2, 19.4 and 18.7%, respectively. The unreported methyl(triethylgermyl)mercury has been prepared by an analogous procedure from (II) and methylmercuric chloride (yield, 79.3% b.p. 75–76°/1.0 mm; d₄²⁰ 1.881). (Found: Hg, 54.10. C₇H₁₈GeHg calcd.: Hg, 53.44%). Among the other reaction products, mercury (100%), chlorotriethylgermane (94.1%), dimethylmercury (traces), and (II) (traces), have been identified. The reaction of (II) with ethylmercuric chloride gave mercury (100%); chlorotriethylgermane (55.2%), diethylmercury (38.0%), (II) (15.2%), and ethyl(triethylgermyl)mercury (53.2%) with b.p. 80–83°/1.0 mm. (Found: Hg, 51.05. C₈H₂₀GeHg calcd.: Hg, 51.51%).

Two new compounds with C–Hg–Ge groupings, n-propyl(triethylgermyl)mercury and isopropyl(triethylgermyl)mercury, were also obtained from the reaction of the corresponding alkylmercuric chlorides with (II) (see *Experimental*). These results suggested that this procedure could provide a simple synthesis for compounds containing C–Hg–Si and C–Hg–Ge groupings.

All the asymmetric silyl- and germyl-mercury compounds are yellow liquids, which can be distilled under reduced pressure. They react instantaneously with air.

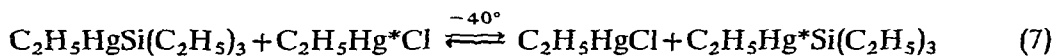
The methods of preparation are themselves strong evidence that the compounds have the RHgE(C₂H₅)₃ structure but chemical evidence has also been obtained. It was shown that these compounds react rapidly and quantitatively with iodine in toluene solution at -40° as shown in eqn. (6).



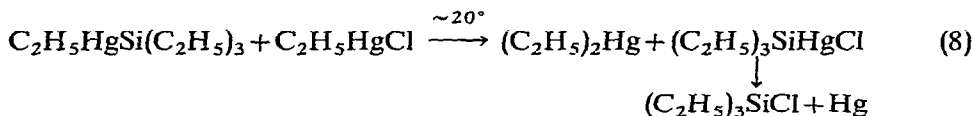
For example, ethyl(triethylgermyl)mercury reacts with iodine to produce ethylmercuric iodide (97.8%) and iodotriethylgermane (92.8%). No metallic mercury was detected. It is known that (II) reacts with an equimolar amount of iodine to give metallic mercury and iodotriethylgermane⁸.

When phenylmercuric chloride was treated with the stoichiometric quantity of (II) at -40° with the object of preparing phenyl(triethylgermyl)mercury, $\text{C}_6\text{H}_5\text{-HgGe}(\text{C}_2\text{H}_5)_3$, the expected product was not obtained in the pure state. The products actually isolated were mercury, chlorotriethylgermane and diphenylmercury, together with a viscous yellow liquid. The yields of the first two products, based on the reactions (5a,b), were 82.1 and 60.0%. The yield of diphenylmercury, based on reactions (5a,c), was 52.9%. Treatment of the yellow liquid with iodine at -40° in toluene produced metallic mercury (see ref. 8), phenylmercuric iodide [see eqn. (6)], and triethyliodogermane. It thus seems probable that this liquid contained (II) and phenyl(triethylgermyl)mercury which could not be separated by vacuum fractionation.

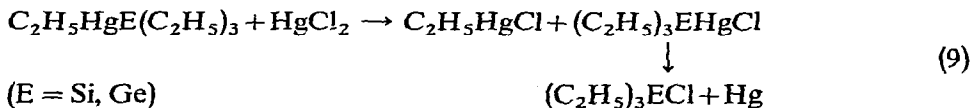
These observations support the idea that reaction (5a) proceeds *via* rapid mercury-for-mercury exchange of halogen and $(\text{C}_2\text{H}_5)_3\text{Si}$ or $(\text{C}_2\text{H}_5)_3\text{Ge}$ groupings. It is reasonable to expect that an exchange of this type also takes place between ethyl-(triethylsilyl)mercury and ethylmercuric chloride at -40° , but in this case the exchange reaction should be reversible and can only be proved by using labelled compounds



When these reactants were allowed to warm to room temperature, metallic mercury, chlorotriethylsilane and diethylmercury were formed. Deposition of mercury is complete at room temperature in about 24 h. The formation of these products in nearly quantitative yields suggests an initial triethylsilyl-ethyl and/or ethyl-chlorine exchange reaction followed by the decomposition of triethylsilylmercuric chloride



Finally, it was found that mercury(II) chloride reacts with ethyl(triethylsilyl)mercury and ethyl(triethylgermyl)mercury, respectively, under mild conditions according to the equation:



After a reaction at -40° for 1 h, 42–48% of the total mercury in the reaction mixture precipitated as metal. The yields of $\text{C}_2\text{H}_5\text{HgCl}$ and $(\text{C}_2\text{H}_5)_3\text{ECl}$, based on the reaction shown in eqn. (9), were 69–94% and 85–91%, respectively.

EXPERIMENTAL

Reactions were carried out in carefully evacuated, sealed ampoules. The composition of the starting mixtures and the separation and identification of the products were carried out without contact of air in the special, previously evacuated apparatus⁹. Triethylchlorosilane and triethylhalogermanes were identified by GLPC (Tsvet-1 Model; column packing, 10% Apiezon L on Chromosorb W; 100–130° program). Dialkylmercury compounds were identified as alkylmercuric iodides by means of the iodine treatment in benzene solution.

Typical experiments are described below.

Reaction of bis(triethylgermyl)mercury(II) with n-propylmercuric chloride

To 6.59 g (0.0127 mole) of (II) maintained at -40° was added, over a period of 1 h, 3.30 g (0.0118 mole) of n-propylmercuric chloride with occasional shaking. The metallic mercury begins to precipitate almost immediately. The mixture was kept at this temperature overnight. The organic layer was decanted from the metallic mercury (2.18 g, 92.0% based on eqns. (5a, b)). The volatiles were vacuum-distilled into a trap cooled with liquid nitrogen. Distillation of the residue *in vacuo* yielded 3.94 g (82.2%) of n-propyl(triethylgermyl)mercury, b.p. $89-90^{\circ}$ (1.5 mm); d_4^{20} 1.811 (found: Hg, 48.81. $C_9H_{22}GeHg$ calcd.: Hg, 49.71%) and 0.69 g (6.8%) of (II), b.p. $116-119^{\circ}$ (1.5 mm); n_D^{20} 1.5694 [lit.⁴ b.p. $118-120^{\circ}$ (1.5 mm); n_D^{20} 1.5696]. The volatiles were treated at about 20° with the benzene iodine solution until the pink colour disappeared. After removal of most of the solvent, n-propylmercuric iodide (trace) was crystallized; m.p. 111° (mixed m.p.). Filtration from the mercurial gave a solution which was analyzed by GLPC. The major product was triethylchlorogermane (76.3%).

Reaction of bis(triethylgermyl)mercury(II) with isopropylmercuric chloride

Following the above procedure, 9.28 g (0.0178 mole) of (II) on treatment with 0.0192 mole of isopropylmercuric chloride gave 4.15 g (100%) of mercury, 3.67 g (98.1%) of triethylchlorogermane, 0.44 g (10.1%) of (II), and 4.93 g (63.8%) of isopropyl(triethylgermyl)mercury, b.p. $75-77^{\circ}$ (1.0 mm); d_4^{20} 1.818. (Found: Hg, 49.09. $C_9H_{22}GeHg$ calcd.: Hg, 49.71%.) No diisopropylmercury was detected.

The other reactions of this type were carried out similarly.

Reaction of ethyl(triethylsilyl)mercury with ethylmercuric chloride

To 7.02 g (0.0204 mole) of ethyl(triethylsilyl)mercury maintained at -40° was added over 1 h with occasional shaking, 5.40 g (0.0204 mole) of ethylmercuric chloride. There was no deposition of metallic mercury. After 2 h, the mixture was warmed to room temperature and left to stand overnight. The organic layer was decanted from the metallic mercury (3.62 g, 88.6% based on eqn. (8)) and was vacuum-distilled into a trap cooled with liquid nitrogen. Diethylmercury was identified as ethylmercuric iodide by means of the iodine treatment of the organic layer in benzene solution at 20° . This was filtered off (5.72 g, 78.7%), m.p. $177-178^{\circ}$ (mixed m.p.). The mother liquor was analyzed by GLPC. The yield of triethylchlorosilane was 94.8%.

Reaction of ethyl(triethylgermyl)mercury with iodine

To a solution of 4.80 g (0.0123 mole) of ethyl(triethylgermyl)mercury in 20 ml of toluene was added over a period of 0.5 h a solution of 3.00 g (0.0118 mole) of iodine in 20 ml of toluene, the temperature being maintained at -40° . No metallic mercury was precipitated. The volatiles were vacuum-distilled into a trap cooled with liquid nitrogen. The white crystalline residue was recrystallized to give 4.30 g (97.8%) of ethylmercuric iodide, m.p. 178° (mixed m.p.). The volatiles were analyzed by GLPC. The yield of triethyliodogermane was 92.8%.

Reaction of ethyl(triethylgermyl)mercury with mercury(II) chloride

To 7.58 g (0.0195 mole) of ethyl(triethylgermyl)mercury maintained at -40° was added, over a period of 1 h, 5.32 g (0.0196 mole) of mercury(II) chloride with occasional shaking. The mixture was left to stand at this temperature overnight. The organic layer was decanted from metallic mercury (3.24 g, 83.0% based on eqn. (9)) and was analyzed as above. The yield of ethylmercuric chloride was 4.84 g (93.8%), m.p. $197-198^{\circ}$ (mixed m.p.). The yield of triethylchlorogermane was 85.3%.

REFERENCES

- 1 N. S. VYAZANKIN, G. A. RAZUVAEV AND O. A. KRUGLAYA, *Organometal. Chem. Rev. A*, 3 (1968) 323.
- 2 E. N. GLADYSHEV, N. S. VYAZANKIN, E. A. ARKHANGEL'SKAYA, G. A. RAZUVAEV AND S. P. KORNEVA, *Dokl. Akad. Nauk SSSR*, 183 (1968) 338.
- 3 N. S. VYAZANKIN, G. A. RAZUVAEV AND E. N. GLADYSHEV, *Dokl. Akad. Nauk SSSR*, 155 (1964) 830.
- 4 N. S. VYAZANKIN, E. N. GLADYSHEV, S. P. KORNEVA, G. A. RAZUVAEV AND E. A. ARKHANGEL'SKAYA, *Zh. Obshch. Khim.*, 38 (1968) 1803.
- 5 N. S. VYAZANKIN, G. A. RAZUVAEV, E. N. GLADYSHEV AND T. G. GURIKOVA, *Dokl. Akad. Nauk SSSR*, 155 (1964) 1108.
- 6 L. G. MAKAROVA AND A. N. NESMEYANOV, *Methods of Elemento-organic Chemistry. The Organic Compounds of Mercury*, North Holland Publishing Company, Amsterdam, 1967.
- 7 D. SEYFERTH, R. J. CROSS AND B. PROKAI, *J. Organometal. Chem.*, 7 (1967) P20.
- 8 K. KÜHLEIN, W. P. NEUMANN AND H. P. BECKER, *Angew. Chem.*, 79 (1967) 870.
- 9 N. S. VYAZANKIN, G. A. RAZUVAEV, O. A. KRUGLAYA AND G. S. SEMCHIKOVA, *J. Organometal. Chem.*, 6 (1966) 474.