REACTIONS OF bis(TRIETHYLGERMYL)MERCURY WITH FLUORINE-CONTAINING ORGANOMERCURY COMPOUNDS

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One of the important methods for producing organomercury halides RHgX is based on exchange reactions of R_2Hg with mercury halides HgX_2 [1]. It is suggested that these reactions are reversible, but almost entirely shifted in the direction of formation of RHgX [2]. The analogous reactions of bis(triethylgermyl)-mercury (BEGM) [3] and related compounds [4, 5] with mercury halides, judging by the substantial evolution of heat, are more energetically profitable, and their uniqueness lies in the fact that the triethylgermylmercury halides formed $(C_2H_5)_3GeHgX$, in contrast to RHgX, are extremely unstable and break down into mercury and $(C_2H_5)_3GeX$.

We have shown that the exchange reactions of BEGM with ethyl esters of α-mercurated fluoroacetic acids and perfluorodialkylmercury compounds proceed just as uniquely, but with a less pronounced thermal effect:

$$[(C_2H_5)_3Ge]_2Hg + HgX_2 \xrightarrow{a} 2(C_2H_5)_3GeHgX \xrightarrow{b} 2(C_2H_5)_3GeX + 2Hg \tag{1}$$
$$X{=}F, CF(CF_3)_2, CHFCO_2C_2H_5, C(CF_3)_3, CF_2CO_2C_2H_5, CFClCO_2C_2H_5.$$

The exchange reaction with bis-tert-perfluorobutylmercurcy in tetrahydrofuran (THF) at ~ 20° ends in several minutes and gives mercury, as well as triethylfluorogermane (IV) and perfluoroisobutylene, formed in the β-decomposition of tert-perfluorobutyltriethylgermane

$$(C_2H_5)_3GeC(CF_3)_3 \rightarrow (C_2H_5)_3GeF + CF_2 = C(CF_3)_2. \tag{2}$$

Analogously, on the basis of esters of α-mercurated fluoroacetic acids, ethyl esters of triethylgermylfluoroacetic (I), triethylgermyldifluoroacetic (II), and triethylgermylfluorochloroacetic (III) acids were produced according to Eqs. (1a), (1b) (Table 1).

The structure of compounds (I)-(III) was confirmed by the data of the IR and mass spectra. In the IR spectra in the region of 1500-400 cm^{-1}, bands are observed belonging to the fragments $(C_2H_5)_3Ge$ with frequencies about 585 and 545 cm^{-1}. The frequencies of the valence vibrations of C = O are 1755 cm^{-1} in (II) and (III); in (I) a band with a doublet structure (1750 and 1718 cm^{-1}) is observed. The intense absorption bands with frequencies 1200 cm^{-1} in (I), 1280 and 1110 cm^{-1} in (II), and 1260 cm^{-1} in (III) probably belong to the valence vibrations of the C – F bonds. The mass spectra of the compounds contain the ion $(C_2H_5)_3Ge$ (m/e 161 for Ge^{74}) and products of its further fragmentation. The molecular ion is detected only for (III) (m/e 300 for Ge^{74} and Cl^{35}).

Just as with other mercury halides [4], the reaction with HgF_2 in THF proceeds very energetically and is described by Eqs. (1a, b).

The occurrence of a reaction with intermediate formation of $(C_2H_5)_3GeHgX$ is well confirmed for the examples of perfluorodimethyl- and perfluorodiisopropylmercury. It was established that in these cases, depending on the nature of the solvent (or additions of a complex former), the exchange reactions can be

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TABLE 1

Compound		Yield, %*	Bp, °C (p, mm Hg)	n_D^{20}	Gross formula	Found, %				Calculated, %			
Number	formula					C	H	F	Ge	C	H	F	Ge
I	$(C_2H_5)_3GeCHFCOOC_2H_5$	59,7 (84,1)	115—116 (14)	1,4518	$C_{10}H_{21}FGeO_2$	45,28	8,03	7,10	27,62	45,34	8,01	7,17	27,78
I	$(C_2H_5)_3GeCF_2COOC_2H_5$	75,8 (69,6)	106—107 (14)	1,4399	$C_{16}H_{20}F_2GeO_2$	—	—	—	25,85	—	—	—	25,66
III	$(C_2H_5)_3GeCFClCOOC_2H_5$	79,4 (78,6)	119—121 (15)	1,4599	$C_{10}H_{20}ClFGeO_2$	40,11	6,74	6,69	24,19	40,12	6,78	6,68	24,25
IV	$(C_2H_5)_3GeF$ †	76,8 —	70 (55)	1,4218	—	—	—	—	—	—	—	—	—
V	$(C_2H_5)_3GeHgCF_3$	82,0 —	90 (2)	1,5140	$C_7H_{15}HgF_3Ge$‡	—	—	—	—	—	—	—	—
VI	$(C_2H_5)_3GeCF_3$	79,6 —	59—60 (40)	1,3990	$C_7H_{15}F_3Ge$	37,35	6,65	—	—	36,75	6,60	—	—
VII	$(C_2H_5)_3GeHgCF(CF_3)_2$	80,4 (63,5)	100—101 (10)	1,4536	$C_9H_{15}HgF_7Ge$	20,88	3,05	—	14,28	20,42	2,86	—	13,71
VIII	$(C_6H_5)_3GeCF_3$	38,1 —	**	—	$C_{19}H_{1}\,F_3Ge$	—	—	15,26	19,60	—	—	15,28	19,46
IX	$(C_2H_5)_3GeCF(CF_3)COOC_2H_5$	— (78,5)	105—106 (10)	1,4254	$C_{11}H_{20}F_4GeO_2$	39,87	6,11	—	21,64	39,66	6,07	—	21,81

*The yields of the compounds were calculated according to Eq. (1); in parentheses according to Eq. (3).

†The compound was produced in the reaction of bis (triethylgermyl) mercury with HgF_2. According to the data of [15]: T. bp 147-148° (744 mm); n_D^{20} 1.4026.

‡Found: Hg 47.02%, calculated: Hg 46.72%.

**Mp 164-165 (from hexane).

described by Eqs. (1a) or (1a), (1b). Thus, the reaction with perfluorodimethylmercury gives $(C_2H_5)_3Ge\cdot HgCF_3$ (V), if it is conducted in toluene at ~ 20° or a mixture of trifluoromethyltriethylgermane (VI) and mercury, if an equimolar amount of α,α'-dipyridyl is added to the reaction mixture, or if THF is taken as the solvent. Analogously, the reaction with perfluorodiisopropylmercury in toluene leads to perfluoroisopropyl(triethylgermyl)mercury (VII) and mercury. In THF the yield of mercury is increased to 60%, and together with compounds (VII) the reaction mixture contains (IV) and perfluoropropylene, formed in the β-decomposition of perfluoroisopropyltriethylgermane.

In the IR spectra of compounds (V)-(VII), the presence of C–F bonds was established according to the appearance of bands in the region of 1000-1350 cm^{-1} [6]. The frequencies ν_s and ν_{as} of the Ge–C bonds have values of 548 and 592 cm^{-1} (V); 542 and 576 (VI); 540 and 577 cm^{-1} (VII). The NMR spectrum of F^{19} for (VII) consists of two signals. One of them belongs to the CF_3 group ($\delta_F = -8.00$ ppm; $^3J_{FF} = 13$ Hz; $^3J_{Hg^{199}F} = 54.1$ Hz); the other belongs to the CF group ($\delta_F = +128.80$ ppm). The spin–spin interaction constant $^2J_{Hg^{199}F}$ was not measured.

We should mention that the reaction of bis(triphenylgermyl)mercury with perfluorodimethylmercury in THF cannot be brought to completion even with prolonged heating (19 h at 100°). The yields of mercury and trifluoromethyltriphenylgermane (VIII) are correspondingly equal to 78.1 and 38.1%.

Exchange reactions of BEGM with mixed compounds of the ClHgX series, where X = $CF(CF_3)_2$, $CHFCO_2C_2H_5$, $CF_2CO_2C_2H_5$, $CFClCO_2C_2H_5$ and $CF(CF_3)\cdot CO_2C_2H_5$, judging by the pronounced thermal effect, proceed more vigorously in THF than with the compounds of the HgX_2 type, corresponding to them. Evidently, just as in the case of mercury dihalides [4, 5, 8] the exothermic nature of these reactions is due to the rapid process of exchange of $(C_2H_5)_3Ge$ for halogens and subsequent decomposition of the triethylgermylmercury chloride formed according to Eq. (3b)

$$\begin{tikzcd}
{[(C_2H_5)_3Ge]_2Hg + ClHgX} \arrow[r, "a", "THF"'] & (C_2H_5)_3GeHgCl + \arrow[dl, "b"'] & (C_2H_5)_3GeHgX \arrow[d, "c"] \\
(C_2H_5)_3GeCl + Hg & & (C_2H_5)_3GeX + Hg
\end{tikzcd} \tag{3}$$

X=$CF(CF_3)_2$, $CHFCO_2C_2H_5$, $CF_2CO_2C_2H_5$, $CFClCO_2C_2H_5$, $CF(CF_3)CO_2C_2H_5$.

In accordance with this, it was found that in the reaction with $ClHgCF(CF_3)_2$ together with triethylchlorogermane (yield 98.6%), (VII) was obtained. Consequently, the exothermic nature of the reaction cannot be attributed to decomposition of (VII) according to Eq. (3c). In the remaining cases the rates of reactions (3b) and (3c) are more comparable. Therefore, the yields of mercury reach ~ 100% of its total content in the initial reagents, and the other products are triethylchlorogermane and the ester (I) (or its corresponding analog). It is interesting to note that the ethyl ester of α-triethylgermylperfluoropropionic acid (IX), synthesized according to scheme (3), exhibits no tendency for β-decomposition, whereas the analogous compounds $(C_2H_5)_3GeCF(CF_3)_2$ and $(C_2H_5)_3GeC(CF_3)_3$ are unstable under comparable conditions (see above).

In the IR spectrum of compound (IX) the frequencies ν_s and ν_{as} of the Ge–C bond are correspondingly equal to 542 and 587 cm^{-1}; the band of the valence vibration of C=O is split into a doublet 1742 and 1662 cm^{-1}. In the NMR spectrum of F^{19} (IX), two signals are observed, the chemical shifts of which (from CF_3COOH) are equal to – 6.85 ppm (doublet $J_{F_3-F_2}$ = 11.3 Hz) and 120.00 ppm (quadruplet). These signals belong to the CF_3 and CF groups.

As is well known, the nonsymmetrical compounds $(C_2H_5)_3GeHgR$(X), where R = Alk, are thermally stable [9, 10] in contrast to $(C_2H_5)_3GeHgX$ (X = Hal), which decomposes at the moment of formation [3, 9, 10]. An analogous pattern is observed for silicon-containing analogs [4, 5, 9, 10]. From our investigation it follows that compounds of the series $(C_2H_5)_3GeHgX$, where X is an electron attracting fluorine-containing radical, are also unstable. This phenomenon may be due to the fact that in stable compounds (X), both radicals next to the mercury possess the same inductive effect (+I), whereas in $(C_2H_5)_3GeHgX$ the I-effects of the substituents differ in sign. In accord with this interpretation, the compounds $Cl_3Si-HgX$ (X = Br, I), in which the Cl_3Si group [11] and X have the same I-effect, are stable even at increased temperatures [12, 13]. Exceptions to this rule are the compounds $(C_2H_5)_3GeHgCF_3$ (V) and $(C_2H_5)GeHgCF(CF_3)_2$ (VI), which can be explained by the presence of an intramolecular donor–acceptor interaction between the fluorine (at the α-carbon) and mercury atoms. The decrease in the stability of these compounds in contact with donor-type ligands (THF, α, α'-dipyridyl) agrees with this explanation [7].

EXPERIMENTAL METHOD

The initial mixtures were compiled without contact with atmospheric oxygen. The reactions were conducted in evacuated sealed test tubes according to the method of [14]. Typical experiments are cited below.

Reaction of bis(Triethylgermyl)mercury with Perfluorodimethylmercury. A solution of 1.13 g perfluorodimethylmercury in 5 ml of toluene was frozen (liquid nitrogen) and 1.75 g BEGM was added. The mixture was left at ~ 20° until decolorization (12 h). The organic layer was decanted from the mercury (0.09 g; 6.7%) and fractionated under vacuum. We obtained 2.32 g (82.0%) of compound (V).

Under the conditions of the preceding experiment, from a solution of 1.30 g perfluorodimethylmercury, 2.01 g BEGM and 1.21 g α, α'-dipyridyl in 5 ml of toluene (reagent ratio 1:1:1), 1.38 g (89.7%) mercury is obtained. Fractionation of the organic layer yielded 1.20 g (68.2%) of compound (VI) and 0.97 g (80.7%) of unchanged α, α'-dipyridyl with bp. 80° (1 mm). The melting point of the substance in a mixed sample was 71°.

From a solution of 2.18 g perfluorodimethylmercury and 3.21 g BEGM in 3 ml of THF, prepared as indicated above, 0.86 g (34.7%) mercury is isolated after 12 h at ~ 20°. The mixture was heated to 80° (5 h). The yield of mercury was 2.38 g (96.1%). The organic layer was fractionated. We isolated 2.24 g (79.4%) of compound (VI).

Perfluoroisopropyl(triethylgermyl)mercury (VII). A mixture of 2.46 a perfluorodiisopropylmercury and 2.58 g BEGM in 4 ml of toluene was left overnight. In the usual way we isolated 0.20 g (10.4%) of mercury and 4.05 g (80.4%) of compound (VII) under comparable conditions, from 2.58 g perfluorodiisopropylmercury and 2.48 g BEGM in 6 ml of THF we obtained 0.94 g (49.3%) mercury, 1.58 g (31.2%) of compound (VII), and 0.36 g (41.4%) triethylfluorogermane. Perfluoropropylene was detected in a trap cooled with liquid nitrogen by the method of gas–liquid chromatography.

Reaction of bis(Triethylgermyl)mercurcy with bis-Tert-perfluorobutylmercury. A mixture of 2.46 g bis-tert-perfluorobutylmercuryfluorobutylmercury and 2.02 g BEGM in 3 ml of THF, produced as described above was thawed. The exothermic reaction ends in 5-7 min with liberation of 1.52 g (98.9%) mercury. Fractionation of the organic layer yielded 1.16 g (85.0%) triethylfluorogermane (IV) with bp. 81-85° (60 mm); n_D^{20} 1.4200, which agrees with the data of [15]. Perfluoroisobutylene was determined in the trap by the method of gas–liquid chromatography. Under analogous conditions, from 2.05 g BEGM and 0.93 g HgF_2 in 4 ml of THF we obtained 1.53 g (97.5%) mercury and 1.08 g (76.8%) triethylfluorogermane (IV).

Ethyl Ester of Triethylgermylfluoroacetic Acid (I). A mixture of 1.2 g BEGM and 0.95 g $Hg(CHFCOO \cdot C_2H_5)_2$ in 3 ml THF was left overnight at –20° and for 24 h at ~ 20°. In the usual way we isolated 0.88 g (92.7%) mercury and 0.74 g (59.7%) of compound (I).

Compounds (II) and (III) were produced analogously.

Ethyl Ester of α-(Triethylgermyl)perfluoropropionic Acid (IX). From a mixture of 3.66 g BEGM, 2.82 g $ClHgCF(CF_3)COOC_2H_5$, and 4 ml of THF at −50° (1 h) we isolated 2.70 g (95.8%) mercury. In addition, 0.90 g (66.5%) triethylchlorogermane with bp. 66-68° (20 mm); n_D^{20} 1.4640 and 1.82 g (78.5%) of compound (IX) were obtained in the usual way.

Compounds (I)-(III) and (VII) were produced analogously according to reaction (3).

CONCLUSIONS

1. Exchange reactions of bis(triethylgermyl)mercury with fluorine-containing mercury compounds of the HgX_2 or ClHgX type give derivatives of the series $(C_2H_5)_3GeHgX$ [when X = CF_3 and $CF(CF_3)_2$] or decomposition products of the latter — mercury and $(C_2H_5)_3GeX$ (X = F, $C(CF_3)_3$, $CHFCO_2C_2H_5$, $CF_2CO_2C_2H_5$, $CFClCO_2C_2H_5$, and $(CF_3)CO_2C_2H_5$).

2. The compounds $(C_2H_5)_3GeCF(CF_3)_2$, $(C_2H_5)_3GeC(CF_3)_3$, but not $(C_2H_5)_3GeCF(CF_3)CO_2C_2H_5$ readily undergo β-decomposition, forming triethylfluorogermane.

LITERATURE CITED

1. L. G. Makarova and A. N. Nesmeyanov, Methods of Heteroorganic Chemistry [in Russian], Nauka, Rtut' (1965).
2. M. D. Rausch and J. R. Van Wazer, Inorgan. Chem., 3, 769 (1964).
3. V. T. Bychkov, Dissertation [in Russian], Gor'kii (1966).
4. D. Seyferth, R. J. Cross, and B. Prokai, J. Organometal Chem., 7, P20 (1967).
5. A. G. Lee, J. Organometal. Chem., 16, 321 (1969).
6. K. Nakanisi, Infrared Spectra and Structure of Organic Compounds [Russian translation], Mir, (1965), p. 207.
7. A. K. Prokof'ev, V. I. Bregadze, and O. Yu. Okhlobystin, Uspekhi Khimii, 39, 412 (1970).
8. B. I. Petrov, V. P. Polishchuk, L. S. German, O. A. Kruglaya, and N. S. Vyazankin, Dokl. Akad. Nauk SSSR, 193, 1315 (1970).
9. N. S. Vyazankin, E. N. Gladyshev, E. A. Arkhangel'skaya, and G. A. Razuvaev, J. Organometal. Chem., 17, 340 (1969).
10. N. S. Vyazankin, E. N. Gladyshev, E. A. Fedorova, and G. A. Razuvaev, Dokl. Akad. Nauk SSSR, 186, 1082 (1969).
11. J. Knizek, M. Horak, and V. Chvalovsky, Coll. Czechoslov. Chem. Comm. 28, 3079 (1963).
12. G. A. Morano and A. G. MacDiarmid, Inorgan. Nucl. Chem. Letters, 5, 621 (1969).
13. C. R. Better, J. C. Sendra, and G. Urry, Proc. of the 4th Intern. Conference on Organometal. Chem., Bristol, M1 (1969).
14. N. S. Vyazankin, G. A. Razuvaev, O. A. Kruglaya, and G. S. Semchikova, J. Organometal. Chem., 6, 474 (1966).
15. B. M. Gladshtein, I. P. Kulyumin, and L. Z. Soborovskii, Zh. Obshch. Khim., 36, 488 (1966).