

## EXCHANGE REACTIONS OF BIS(TRIETHYLGERMYL)MERCURY. SYNTHESIS OF FLUOROALKYL(TRIETHYLGERMYL)MERCURIALS

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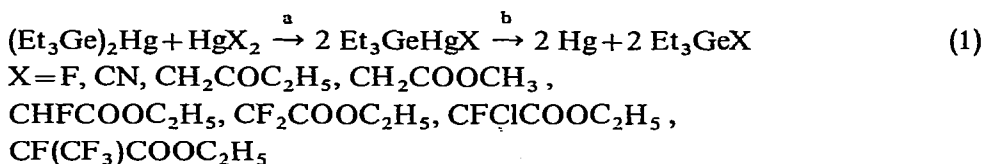
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### SUMMARY

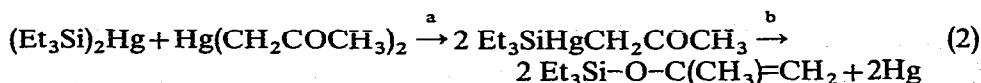
The interaction of  $\text{HgR}_2^f$  [ $\text{R}^f = \text{CF}_3, \text{CH}_2\text{CF}_3, \text{CHFCF}_3, \text{CFCICF}_3, \text{CF}_2\text{CF}_3, \text{CH}(\text{CF}_3)_2, \text{CF}(\text{CF}_3)_2$ ] with bis(triethylgermyl)mercury in benzene results in a high yield of the corresponding fluoroalkyl(triethylgermyl)mercurials,  $\text{Et}_3\text{GeHgR}^f$ , which are thermally stable liquids capable of vacuum distillation. In the presence of catalytic amounts of CsF in THF these compounds decompose at room temperature to yield metallic mercury and  $\text{Et}_3\text{GeR}^f$ , the latter eliminating  $\text{Et}_3\text{GeF}$  when  $\text{R}^f$  is  $\text{CH}(\text{CF}_3)_2$  or  $\text{CF}(\text{CF}_3)_2$ . The mechanism of fluoride ion catalysis is discussed.

### INTRODUCTION

Bis(triethylgermyl)mercury is known to exchange with mercury derivatives of the type  $\text{HgX}_2$  (where X stands for an electron-accepting atom or radical) under mild conditions<sup>1-4</sup>. The formation of unsymmetrical mercurials is followed by their decomposition, so that the reaction is irreversible.



Bis(trimethylsilyl)mercury reacts similarly with  $\text{HgX}_2$ , when X is Cl, Br, I, or  $\text{CN}^{5-7}$ . With  $\alpha$ -mercurated ketones, which exhibit a dual reactivity, reactions with bis(trimethylsilyl)- and bis(triethylgermyl)mercury is accompanied by transfer of the reaction centre, such rearrangement apparently taking place at the demercuration stage<sup>8</sup>, e.g.



All these reactions proceed rapidly in THF and are exothermal, especially in the case where X is F, Cl, Br, I or CN.

The reaction of bis(triethylgermyl)mercury and  $(C_6F_5)_2Hg$  in THF is somewhat more specific since at room temperature stage (1a) of the reaction is completed in several minutes, while demercuration of pentafluorophenyl(triethylgermyl)mercury [eqn. (1b)] is completed only after prolonged heating at  $100^\circ$ .

In this paper radical-exchange reactions between bis(triethylgermyl)mercury and the bis(polyfluoroalkyl)mercurials  $HgR_2^f$ , where  $R^f$  are electron-accepting fluoroalkyl groups, are discussed.

#### EXPERIMENTAL

All reactions were carried out in evacuated sealed ampoules following the technique described in Ref. 9. The conditions for radical-exchange reactions are listed in Table 1. The conditions for, and products of, catalytic decomposition of fluoroalkyl-(triethylgermyl)mercury compounds in the presence of CsF are presented in Table 2.

Typical experiments are given below.

TABLE 1

REACTIONS OF BIS(TRIETHYLGERMYL)MERCURY WITH  $HgR_2^f$  IN BENZENE

$(Et_3Ge)_2Hg$ (g)	$HgR_2^f$ (g)	Benzene (ml)	Reaction conditions Temp. ( $^\circ$ ) Time (h)		Reaction product B.p. ( $^\circ C/mm$ ) (Yield, %)	$n_D^{20}$	Analysis found (calcd.) (%)
1.75	$Hg(CF_3)_2$ (1.13)	5	20	12	$Et_3GeHgCF_3$ 101–102/5 (82)	1.5140	47.02 (46.72)
2.1	$Hg(CH_2CF_3)_2$ (1.6)	5	100	50 <sup>a</sup>	$Et_3GeHgCH_2CF_3$ 110–112/10 (63)	1.4990	44.85 (45.23)
2.7	$Hg(CHFCF_3)_2$ (2.1)	5	100	52 <sup>b</sup>	$Et_3GeHgCHFCF_3$ 117–118/10 (82)	1.4957	43.13 (43.46)
2.1	$Hg(CF_2CF_3)_2$ (1.8)	5	20	48	$Et_3GeHgCF_2CF_3$ 108–109/10 (77)	1.4798	41.38 (41.91)
1.45	$Hg(CFCICF_3)_2$ (1.3)	3	20	24	$Et_3GeHgCFCICF_3$ 123–125/10 (76)	1.5018	<sup>c</sup>
1.54	$Hg[CH(CF_3)_2]_2$ (1.52)	3	20	144	$Et_3GeHgCH(CF_3)_2$ 107–108/10 (82)	1.4660	38.87 (39.22)
2.58	$Hg[CF(CF_3)_2]_2$ (2.46)	4	20	24	$Et_3GeHgCF(CF_3)_2$ 100–101/10 (80)	1.4536	<sup>d</sup>

<sup>a</sup> The mixture was additionally irradiated with a 150 W incandescent lamp for 63 h at  $20^\circ$ . <sup>b</sup> The same, for 54 h at  $20^\circ$ . <sup>c</sup> (Found: C, 19.74; H, 3.16; F, 15.45;  $C_9H_{15}ClF_4GeHg$  calcd.: C, 19.44; H, 3.04; F, 15.42%) <sup>d</sup> (Found: C, 20.88; H, 3.05; Ge, 14.28;  $C_9H_{15}F_7GeHg$  calcd.: C, 20.42; H, 2.86; Ge, 13.71%)

TABLE 2

CATALYTIC DECOMPOSITION OF  $\text{Et}_3\text{GeHgR}^f$  IN THF UNDER THE INFLUENCE OF  $\text{CsF}^a$ 

Compound (g)	CsF (g)	THF (ml)	Products (yield, %)	Mass-spectrometric data (for triethyl perfluoroalkylgermane) obtained ( <i>m/e</i> , fragment)
$\text{Et}_3\text{GeHgCF}_3$ 1.90	0.41	4	Hg, 92; $\text{Et}_3\text{GeCF}_3$ , 70 <sup>b</sup>	230, M; 201, $\text{Et}_2\text{GeCF}_3$ ; 180, $\text{Et}_2\text{GeF}$ ; 173, $\text{EtGeHCF}_3$ ; 161, $\text{Et}_3\text{Ge}$ ; 151, $\text{Et}_2\text{GeF}$ ; 133, $\text{Et}_2\text{GeH}$ ; 123, $\text{EtGeHF}$ ; 105, $\text{EtGeH}_2$ ; 103, $\text{EtGe}$ ; 93, $\text{GeF}$ ; 75, $\text{GeH}$ ; 74, $\text{Ge}$ .
$\text{Et}_3\text{GeHgCH}_2\text{CF}_3$ 2.87	0.25	4	Hg, 25; other products	
$\text{Et}_3\text{GeHgCHFCF}_3$ 2.10	0.28	4	Mixture of 30 $\text{Et}_3\text{GeCHFCF}_3$ and 70 $\text{Et}_3\text{GeF}^c$	262, M; 242, M-HF; 233, $\text{Et}_2\text{GeC}_2\text{F}_4\text{H}$ ; 213, $\text{Et}_2\text{GeC}_2\text{F}_3$ ; 203, $\text{EtGeC}_2\text{F}_4$ ; 180, $\text{Et}_3\text{GeF}$ ; 161, $\text{Et}_3\text{Ge}$ ; 151, $\text{Et}_2\text{GeF}$ ; 133, $\text{Et}_2\text{GeH}$ ; 123, $\text{EtGeHF}$ ; 103, $\text{EtGe}$ ; 93, $\text{GeF}$ ; 75, $\text{GeH}$ ; 74, $\text{Ge}$ .
$\text{Et}_3\text{GeHgCF}_2\text{CF}_3$ 1.65	0.45	4	Hg, 88; $\text{Et}_3\text{GeCF}_2\text{CF}_3$ <sup>d</sup> , 75	251, $\text{Et}_2\text{GeC}_2\text{F}_5$ ; 203, $\text{EtGeC}_2\text{F}_4$ ; 180, $\text{Et}_3\text{GeF}$ ; 161, $\text{Et}_3\text{Ge}$ ; 151, $\text{Et}_2\text{GeF}$ ; 133, $\text{Et}_2\text{GeH}$ ; 123, $\text{EtGeHF}$ ; 103, $\text{EtGe}$ ; 93, $\text{GeF}$ ; 75, $\text{GeH}$ ; 74, $\text{Ge}$ .
$\text{Et}_3\text{GeHgCFCICF}_3$ 2.22	0.31	4	Hg, 98; $\text{Et}_3\text{GeCFCICF}_3$ <sup>e</sup> , 75	267, M-Et; 231, M-Cl; 219, $\text{GeCFCICF}_3$ ; 203, $\text{Et}_2\text{GeCFCF}_3$ ; 180, $\text{Et}_3\text{GeF}$ ; 161, $\text{Et}_3\text{Ge}$ ; 151, $\text{Et}_2\text{GeF}$ ; 133, $\text{Et}_2\text{GeH}$ ; 123, $\text{GeHF}$ ; 105, $\text{EtGeH}_2$ ; 103, $\text{EtGe}$ ; 93, $\text{GeF}$ ; 75, $\text{GeH}$ ; 74, $\text{Ge}$ .
$\text{Et}_3\text{GeHgCH}(\text{CF}_3)_2$ 1.71	0.30	3	Hg, 91; $\text{Et}_3\text{GeF}$ , 81; $\text{CF}_2=\text{CHCF}_3$ <sup>f</sup>	
$\text{Et}_3\text{GeHgCF}(\text{CF}_3)_2$ 1.62	0.31	4	Hg, 92; $\text{Et}_3\text{GeF}$ , 75; $\text{CF}_2=\text{CFCF}_3$ <sup>f</sup>	

<sup>a</sup> The reactions are complete at room temperature after 3–5 min. In case of  $\text{Et}_3\text{GeHgCH}_2\text{CF}_3$ , the mixture was analysed after 72 h at 20°. <sup>b</sup> <sup>19</sup>F NMR spectrum: singlet  $\text{CF}_3$  at  $-22.7$  ppm (external  $\text{CF}_3\text{COOH}$ ). <sup>c</sup> <sup>19</sup>F NMR spectrum:  $\delta(\text{CF}_3) - 5.62$ ,  $\delta(\text{CF}) + 157.2$  ppm,  $J(\text{CF}_3-\text{F}) 16.6$ ,  $J(\text{CF}_3-\text{H}) 11.4$ ,  $J(\text{H}-\text{F}) 45.1$  Hz. <sup>d</sup> B.p. 70°/45 mm;  $n_D^{20} 1.3851$ ; <sup>19</sup>F NMR spectrum: two single broadened signals  $\delta(\text{CF}_3) + 5.76$ ,  $\delta(\text{CF}_2) + 46.0$  ppm. (Found: C, 34.53; H, 5.47; F, 33.75.  $\text{C}_8\text{H}_{15}\text{F}_5\text{Ge}$  calcd.: C, 34.47; H, 5.42; F, 34.06%) <sup>e</sup> See experimental. <sup>f</sup> Identified by GLC techniques.

### 1-Chloro-1,2,2,2-tetrafluoroethyl(triethylgermyl)mercury

To a preliminarily degassed solution of  $\text{Hg}(\text{CFCICF}_3)_2$  (1.32 g, 28.0 mmol) in 3 ml of benzene in an evacuated ampoule bis(triethylgermyl)mercury (1.45 g, 27.9 mmol) was added. The mixture was kept at room temperature for 24 h, the characteristic yellow colour of the germylmercury compound having disappeared. Only traces of metallic mercury could be detected. The fractionation of the reaction mixture gave the desired product (2.11 g, 76%), b.p. 123–125°/10 mm,  $n_D^{20} 1.4957$ . (Found: C, 19.74; H, 3.16; F, 15.45.  $\text{C}_8\text{H}_{15}\text{ClF}_4\text{GeHg}$  calcd.: C, 19.44; H, 3.04; F, 15.42%.)

### Triethyl(1-chloro-1,2,2,2-tetrafluoroethyl)germane

Finely-dispersed anhydrous  $\text{CsF}$  (0.31 g, 2.0 mmol) in 4 ml of THF was degassed, frozen with liquid nitrogen and  $\text{Et}_3\text{GeHgCFCICF}_3$  (2.22 g, 4.6 mmol) was added. During the course of subsequent defrosting mercury was eliminated (0.88 g, 98%). At room temperature the reaction was completed after 3–5 min. The organic layer was

fractionated to obtain the desired product (1.03 g, 78%), b.p. 85–88°/45 mm,  $n_D^{20}$  1.4150. (Found: C, 32.44; H, 4.86; F, 26.09.  $C_8H_{15}ClF_4Ge$  calcd.: C, 32.55; H, 5.12; F, 25.73%.)  $^{19}F$  NMR-spectrum (external  $CF_3COOH$ ): doublet,  $\delta(CF_3)$  0.28 ppm; quartet,  $\delta(CF)$  67.25 ppm;  $J(F-F)$  9.9 Hz. IR-spectrum: 1680 w, 1470 s, 1432 m, 1385 m, 1355 m, 1315 (sh), 1280 s, 1200 s, 1180 vs, 1100 m, 1030 s, 980 m, 945 (sh), 905 (sh), 866 m, 714 s, 625 (sh), 594 s, 546 m.

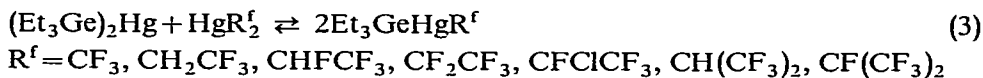
#### *Interaction of ethyl(triethylgermyl)mercury with fluoride ion*

Under the same conditions as described above,  $Et_3GeHgEt$  (5.14 g, 13.2 mmol) was added to a mixture of  $CsF$  (0.31 g, 2.1 mmol) in 4 ml of THF. The mixture was kept at room temperature for 3 days. The volatile products were isolated from the reaction mixture by vacuum recondensation. By fractionating the yellow-coloured residue, unreacted  $Et_3GeHgEt$  (3.21 g, 62%) was obtained and bis(triethylgermyl)mercury separated (0.63 g, 48%), b.p. 119–122°/1 mm. (Found: Hg, 38.61; 38.64.  $C_{12}H_{30}Ge_2Hg$  calcd.: Hg, 38.56%.) To determine the  $Et_2Hg$  yield, the volatile fraction was treated at 0° with a benzene solution of iodine. Ethylmercury iodide (0.43 g, 48%) was isolated and identified by conventional techniques.

#### RESULTS AND DISCUSSION

As may be seen from the data presented in Table 1, fluorinated dialkylmercurials  $HgR_2^f$  react with bis(triethylgermyl)mercury in benzene in 1/1 ratio, giving the corresponding fluoroalkyl(triethylgermyl)mercurials in high yields.

These reactions are, evidently, reversible, but the equilibrium is strongly shifted to the right:



As is well known, radical-exchange reactions in organometallic compounds proceed more readily the greater the difference between the electronegativity of the exchanging radicals<sup>10</sup>. Thus, with  $Hg(CH_2CF_3)_2$  and  $Hg(CHF_2CF_3)_2$  the reactions depicted in eqn. (3) proceed under more severe conditions (100°) than those required for  $Hg(CF_3)_2$  and  $Hg[CF(CF_3)_2]_2$  which react with bis(triethylgermyl)mercury at room temperature. It is evident that bis(trimethylsilyl)mercury does not exchange with dimethylmercury at 20°<sup>7</sup> for the same reason. In these mercurials the inductive effect of both the radicals (*i.e.*  $Me_3Si$  and  $Me$ ) is positive. On the other hand, bis(trichlorosilyl)mercury,  $(Cl_3Si)_2Hg$ , under approximately the same conditions reacts with  $Et_2Hg$ , giving ethyl(trichlorosilyl)mercury<sup>11</sup>. In this case, the  $Cl_3Si$ -group is known to have  $-I$  effect<sup>12</sup>, while the  $Et$ -group is an electron-donating substituent.

The differences between the exchange reactions depicted in eqns. (3) and (1) are as follows:

(i). The reaction of bis(triethylgermyl)mercury with  $HgR_2^f$  is much less vigorous than with  $HgX_2$  compounds.

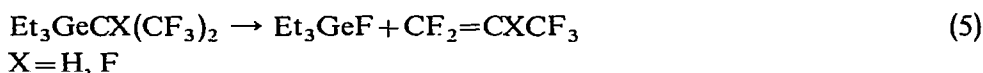
(ii). The demercuration reaction (1b) does not occur with  $Et_3GeHgR^f$ . The latter compounds are stable colourless liquids, distillable *in vacuo*. On the other hand, compounds of the  $Et_3GeHgX$  series are extremely unstable, and their possible formation as intermediates in reaction (1) can only be postulated.

Such a considerable difference between the above reactions cannot be attributed solely to the difference between the electronegativities of the  $R^f$  and X substituents in the mercury compounds. Thus, despite the fact that the electronegativity values of  $CF_3$  and Cl are similar<sup>13</sup>, the reaction of bis(triethylgermyl)mercury with  $HgCl_2$  is exothermal and takes several minutes for the quantitative formation of mercury and triethylchlorogermane, whereas the reaction with  $Hg(CF_3)_2$  is not exothermal, proceeds slowly, and, as can be seen from Table 1, corresponds to eqn. (3).

The peculiarities of reaction (3) may be explained from the assumption that in  $-Hg-R^f$  groupings there exists an intramolecular donor/acceptor interaction  $F-Hg$ , which compensates to a certain extent for the electron attraction of  $R^f$ . This effect opposes the radical exchange process and enhances the stability of the  $Et_3GeHgR^f$  formed. On the other hand, factors which disturb the intramolecular coordination between mercury and fluorine atoms should cause a sharp reduction in the stability of  $Et_3GeHgR^f$ . In accord with this latter viewpoint, we have found that fluoride ions catalyse the decomposition of fluoroalkyl(triethylgermyl)mercurials in THF. At room temperature the reaction takes several minutes with a practically quantitative elimination of mercury.



In the case of  $Et_3GeHgCH(CF_3)_2$  and  $Et_3GeHgCF(CF_3)_2$  the reaction is followed by decomposition of the  $Et_3GeR^f$  formed:



This latter process is also probably influenced by fluoride ions, since the organotin analogues,  $Me_3SnCH(CF_3)_2$  and  $Me_3SnCF(CF_3)_2$ , are known to possess high thermal stability<sup>14</sup>. Moreover,  $Me_3GeCF_3$ <sup>15</sup> and  $Me_3SnCF_3$ <sup>16</sup> demonstrate the higher stability of the germanium derivatives. It is also known that the formation of difluorocarbene from  $Me_3SnCF_3$  under the influence of iodide ions proceeds under mild conditions<sup>17</sup>.

In the case of  $Et_3GeHgCH_2CF_3$  catalytic demercuration is slow (see Table 2), which can be explained by the low electron-withdrawing effect of the  $R^f$  group. For ethyl(triethylgermyl)mercury, in which both substituents at the mercury atom have +I effect, catalytic decomposition is not at all characteristic. It should be noted, however, that fluoride ions cause symmetrisation of these compounds to diethylmercury and bis(triethylgermyl)mercury.

The catalytic function of the fluoride ion in reaction (4) is essentially the same as in the reaction of the bis(perfluoroalkyl)mercurials  $R^f-Hg-R^f$ , where the nucleophilic coordination of  $F^-$  with the Hg atom substantially enhances the carbanion character of the  $R^f$  groups. In this case the nucleophilic catalysis effect is also greater when no intramolecular coordination occurs between F and Hg atoms, which results in a much greater lability of the  $(CF_3)_3C$  group in comparison with the  $(CF_3)_2CF$  group<sup>18</sup>.

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