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PENTAFLUOROPHENYLGERMYLBISMUTH COMPOUNDS

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Summary

Triethylbismuth reacts with $(C_6F_5)_3GeH$ to give $(C_6F_5)_3GeBiEt_2$ and $[(C_6F_5)_3Ge]_2BiEt$ and with $(C_6F_5)_2GeH_2$ to give $[(C_6F_5)_2GeBiEt]_2$. The presence of C_6F_5 radicals does not increase the stability of $(C_6F_5)_3M{-}Bi\lessdot$ compounds (M = Ge, Sn). Their reactivity in the transmetallation reaction with mercury has been studied.

Introduction

On examination of the properties of pentafluorophenyl compounds $[(C_6F_5)_3M]_nM'$ [where M = Si, Ge, Sn; M' = transition and non-transition metal (or non-metal)] we have come to the conclusion that the intramolecular coordination of the unshared electron pairs of *ortho*-fluorine atoms in C_6F_5 rings to appropriate vacant orbitals of the central heteroelement M' may be responsible for stabilization of such compounds in some cases and destabilization in others. In the compounds where M' has such orbitals and is an active metal (e.g. Li), *o*-F → M' coordination results in compound destabilization [1—3] due to the readily proceeding elimination of M'F. If M' is less active (e.g. Hg, Pt), then the effect specified above increases the stability of the compound [4—6]. Finally, if M' does not tend to act as the acceptor of *p*-electrons (e.g. S, Se, Te), then *o*-F → M' coordination is very weak or not present, and hence the stability of the compound in this case is determined by all the other factors that are typical of non-fluorinated analogs [7,8]. In this connection it was interesting to study properties of pentafluorophenyl-germyl and -stannyl derivatives of bismuth. Our earlier attempts to synthesize such compounds via the reaction of bismuth chloride and $(C_6F_5)_3GeGeEt_3$ were unsuccessful [3]. In the present paper we report on the new compounds with a $C_6F_5{-}Ge{-}Bi$ group obtained by a hydride method.

Results and discussion

The reaction of tris(pentafluorophenyl)germane with triethylbismuth proceeds in the absence of a solvent according to eq. 1. The first ethyl group is substituted

$$n(C_6F_5)_3GeH + Et_3Bi \rightarrow [(C_6F_5)_3Ge]_nBiEt_{3-n} + nEtH \qquad (1)$$

$$\text{(I, II)}$$

(I, $n = 1$; II, $n = 2$)

at 90—100°C. Heating up to 170°C leads to the formation of disubstituted compound II. We were not successful in substituting the third Et group as further heating resulted in decomposition of the compound with the precipitation of Bi. It should be noted that in similar reactions at 140°C triethyl- and triphenyl-germane give $(R_3Ge)_3Bi$ in good yields [9,10]. The differences observed between phenyl and pentafluorophenyl compounds may be accounted for by, (i) increased steric hindrance on substitution of two ethyl groups by bulky $(C_6F_5)_3$-Ge fragments or (ii) a sharp decrease in reactivity of the remaining Bi—Et bonds towards the attacking hydride, caused by the strong electron-withdrawing effect of $(C_6F_5)_3Ge$ groups bonded to bismuth. The latter seems to be the main reason, because on heating to 150°C compounds I and II do not react with triethylgermane. The higher temperature causes the decomposition of the compounds.

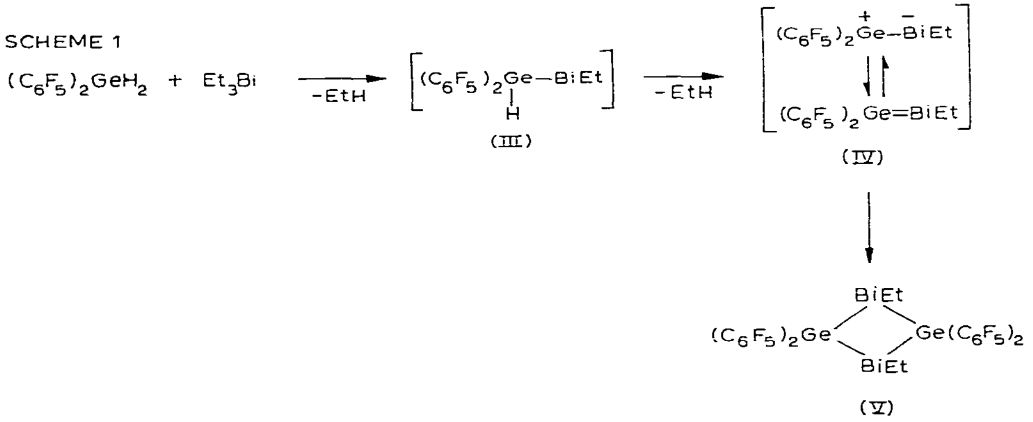
Though we have previously been successful in synthesizing $[(C_6F_5)_3M]_2E$ (M = Ge, Sn; E = Hg, S, Se, Te) [4,5,7,8], all attempts to obtain $[(C_6F_5)_3Ge]_3Bi$ by exchange reaction of $(Et_3Ge)_3Bi$ and $(C_6F_5)_3GeBr$ failed. The reaction products are hexakis(pentafluorophenyl)digermane (54%), triethylgermanium bromide (73%) and bismuth (68%) (eq. 2).

$$6\ (C_6F_5)_3GeBr + 2\ (Et_3Ge)_3Bi \rightarrow 3\ (C_6F_5)_6Ge_2 + 6\ Et_3GeBr + 2\ Bi \qquad (2)$$

Tris(pentafluorophenyl)tin hydride reacts with Et_3Bi under milder conditions (70—90°C) than $(C_6F_5)_3GeH$ and Ph_3SnH, however, the monosubstituted product $(C_6F_5)_3SnBiEt_2$ formed is extremely unstable, unlike the analogous non-fluorinate compounds [9,11]. Therefore, we did not succeed in isolating it or substituting the second and the third ethyl groups.

The reaction of triethylbismuth with bis(pentafluorophenyl)germane proceeds in a very interesting manner. Slow heating of the equimolar mixture of these compounds is accompanied by smooth evolution of ethane within the temperature range 60—105° C. 50% of the gas evolves at 60—95° C and the reaction mixture turns dark red. On careful increasing the temperature the rest of the ethane is liberated and the mixture turns dark cherry and solidifies. If the mixture is heated quickly from 95—105°C or slightly overheated (up to 110° C) the second step of the reaction proceeds very violently. Separation of the product by crystallization from benzene gives a bright orange crystalline compound. Elemental analysis and the IR spectrum suggests the resultant product has the general formula $(C_6F_5)_2GeBiEt$. Determination of the molecular weight (cryoscopy in benzene) has shown the compound to be dimeric and hence it should contain a four-membered germanium—bismuth heterocycle $\overset{|}{Ge}—Bi—Ge—\overset{|}{Bi}$. The yield of $[(C_6F_5)_2GeBiEt]_2$ (30—60%) is barely affected by the molar ratio of the reagents in the initial mixture. The conditions of the reaction are of greater importance: the yield of the product increases on rapid heating of the reaction mixture and the second step proceeds violently. Along with this compound the reaction yields a viscous dark cherry uncrystallizable and undistillable liquid, which is likely to be a mixture of multimember heterocyclic products, $[(C_6F_5)_2GeBiEt]_n$. The following reaction Scheme 1 may be supposed according to the data obtained. We failed to isolate the unstable intermediate III but the

SCHEME 1



formation of it is confirmed by appearance of a new band due to Ge—H stretching mode at 2060 cm^{-1} * in the IR spectrum of the reaction mixture, which is formed after the first low-temperature reaction step 60—95°C is over. On completion of the reaction the band disappears. Intramolecular elimination of ethane and formation of the ylide intermediate (IV) are evidenced by the nature of the reaction as well as by the fact that the formation of the product V is still observed at room temperature for 15—20 minutes after ethane liberation is complete. We note that the formation of analogous ylide intermediate $[R_2\overset{+}{S}i—\overset{-}{N}R']$ has recently been proposed to explain the reaction of aminofluorosilane $R_2Si(F)—N(H)R'$ with butyllithium [13].

Evolution of ethane in the second step of the reaction between $(C_6F_5)_2GeH_2$ and Et_3Bi might also be due to intermolecular processes which apparently lead to cyclic oligomers, $[(C_6F_5)_2GeBiEt]_n$. However, attempts to obtain a linear oligomer according to the reaction 3 failed. Products II and V have been isolated

$$(C_6F_5)_2GeH_2 \xrightarrow[60-90^\circ C]{2\ Et_3Bi} [(C_6F_5)_2Ge(BiEt_2)_2] \xrightarrow[70-140^\circ C]{2\ (C_6F_5)_3GeH} \not\rightarrow$$

$$(C_6F_5)_3Ge—BiEt—Ge(C_6F_5)_2—BiEt—Ge(C_6F_5)_3 \qquad (3)$$

from the final reaction mixture only.

The relative qualitative air stability of the germylbismuth compounds was V >> II > I. Cyclic product V is not oxidised in the crystalline state or in solution, the compound II is stable in the crystalline state only and the monosubstituted product I is oxidised in air at a pronounced rate in solution or in the

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* In the initial $(C_6F_5)_2GeH_2$ ν(Ge—H) is 2142 cm^{-1} [12].

crystalline state. IR spectra of the products have low intensity bands due to the Et—Bi group (in the range 670—620 cm^{-1}) along with the absorption bands of C_6F_5—Ge fragments. To confirm the structure of the compounds their reactions with bromine and hydrogen chloride were carried out which gave the expected products in good yields (eq. 4—7). The high chemical stability of V is noteworthy

$$[(C_6F_5)_3Ge]_nBiEt_{3-n} \xrightarrow{3\,Br_2} n\,(C_6F_5)_3GeBr + BiBr_3 + 3 - n\,EtBr \quad (4)$$

(I, II)

$$[(C_6F_5)_3Ge]_nBiEt_{3-n} \xrightarrow{n\,HCl} n\,(C_6F_5)_3GeH + Cl_nBiEt_{3-n} \quad (5)$$

$(n = 1, 2)$

$$[(C_6F_5)_2GeBiEt]_2 \xrightarrow{6\,Br_2} 2\,(C_6F_5)_2GeBr_2 + 2\,BiBr_3 + 2\,EtBr \quad (6)$$

(V)

$$[(C_6F_5)_2GeBiEt]_2 \xrightarrow{2\,HCl} 2\,(C_6F_5)_2Ge(H)Cl + 2\,Bi + (?) \quad (7)$$

Its reaction with HCl at room temperature takes more than three days. The behaviour of ethyl radicals in this reaction is still unknown.

Thus, we can conclude that the presence of C_6F_5 substituents, as was expected, does not increase the stability of $(C_6F_5)_3M$—Bi$<$ compounds compared to their non-fluorinated analogues. Unfortunately we cannot compare the properties of V with those of $[(C_6H_5)_2GeBiR]_2$ since the latter are unknown.

After synthesising pentafluorophenyl—Ge—Bi compounds we intended to use them transmetallation reactions to obtain derivatives of other metals. We believe that one of the main factors influencing the shift of equilibrium in the processes R—M + M′ $\rightleftharpoons$ R—M′ + M is a relative difference in ionization potentials of M and M′ metals. When the substituent R is electronegative and other conditions are approximately equal the equilibrium shifts more to the right the greater $I_M - I_{M'}$ is. This point of view is in accordance with transmetallation reaction mechanism proposed in the literature [14]. Of all metals bismuth has the highest ionization potential, therefore it was expected that germylbismuth compounds containing electronegative $(C_6F_5)_3Ge$ substituents would display high reactivity in transmetallation reactions similarly to $(C_6F_5)_3Bi$ [15] and would be a useful starting material for obtaining other compounds of the $[(C_6F_5)_3Ge]_nM$ series. Since we have not managed to obtain $[(C_6F_5)_3Ge]_3Bi$, the activity of mono- and di-germyl derivatives I and II in transmetallation reactions has been studied. Compound I was not found to react with metallic mercury in THF (20°C, 6 d). Under the same conditions the compound II gave bis[tris(pentafluorophenyl)germyl]mercury (yield 61%) (eq. 8).

$$3\,[(C_6F_5)_3Ge]_2BiEt + Hg \rightarrow 3\,[(C_6F_5)_3Ge]_2Hg + 2\,Bi + BiEt_3 \quad (8)$$

We think these data confirm the above mentioned assumption about the effect of metal ionization potentials upon the shifting of the equilibrium in such processes. At the same time the preparative possibilities of II are limited due to the presence of the Bi—Et group.

Experimental

All experiments were carried out in evacuated systems. The synthesis of I, II and III was performed while steadily removing the evolved ethane to a gas burette. GLC analysis was carried out on a Tsvet-104 chromatograph with a catharometer detector, using columns (50 × 0.4 cm and 100 × 0.4 cm).packed with OV-17 (7%) on Chromatone N-AW-DMCS, and helium as carrier gas. IR spectra were recorded on a UR-20 spectrophotometer. The melting points of the compounds are given without correction.

Diethyl[tris(pentafluorophenyl)germyl]bismuth (I)

2.4 g (8.11 mmol) of triethylbismuth was added to 4.7 g (8.19 mmol) of $(C_6F_5)_3GeH$. The mixture turns light brown at room temperature. On heating the mixture to 70°C ethane was evolved. Then over 30 min the temperature was gradually increased to 110°C and maintained for 30 min. 178 ml (98%) of ethane evolved. The resulting mixture was dissolved in toluene and 0.05 g (3%) of metallic bismuth precipitated which was separated by decantation. Toluene was removed from the solution by recondensation in vacuo and the residue was recrystallized from hexane. Light yellow crystals of compound I (5.15 g, 75%), m.p. 92—94°C, were obtained. (Found *: C, 32.16; H, 1.13; Bi, 24.88. $C_{22}H_{10}BiF_{15}Ge$ calcd.: C, 31.43; H, 1.19; Bi, 24.85%.)

Ethyl{bis[tris(pentafluorophenyl)germyl]}bismuth (II)

A mixture of tris(pentafluorophenyl)germane (3.36 g, 5.82 mmol) and Et_3Bi (0.88 g, 2.97 mmol) was heated from 70—120°C for 30 min, 65 ml of ethane was evolved. Further heating at 170°C for 1 h resulted in the liberation of 60 ml of gas. The total yield of ethane was 125 ml (96%). After separation of metallic bismuth (0.05 g, 8%), as described above, the product was recrystallized from toluene. The compound II had m.p. 148—150°C; yield 2.92 g (72%). (Found: C, 33.34; H, 0.72; Bi, 14.36. $C_{38}H_5BiF_{30}Ge_2$ calcd.: C, 32.94; H, 0.36; Bi, 15.08%.)

Reaction of tris(pentafluorophenyl)germanium bromide with $(Et_3Ge)_3Bi$

Mixture of tris(triethylgermyl)bismuth (1.04 g, 1.51 mmol) and $(C_6F_5)_3GeBr$ (3.05 g, 4.66 mmol) was heated for 3.5 h at 130°C. The resulting Et_3GeBr (0.8 g, 73%) was removed by condensation in vacuo. The residue was washed with hot toluene and THF heated in vacuo (210—220°C/0.1 mmHg). 1.45 g (54%) of $(C_6F_5)_6Ge_2$ was sublimated, m.p. (mixed) 308—312°C. After sublimation 0.3 g (68%) of metallic bismuth was obtained.

Reaction of bis(pentafluorophenyl)germane with triethylbismuth

Smooth ethane evolution is observed on heating the mixture of $(C_6F_5)_2GeH_2$

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* The presence of bismuth hinders the determination of the fluorine content in the compounds.

(1 g, 2.45 mmol) and triethylbismuth (0.74 g, 2.6 mmol) at 70°C. The temperat was raised for 20 min to 90°C. During this time the yield of ethane reaches 50% and the reaction slows down. When the temperature is raised to 100—110°C further gas liberation proceeds very vigorously. In 30—60 s, the yield of gas is 108 ml (99%). The solid formed was dissolved by heating in 10 ml of benzene. After centrifugation the solution was decanted from traces of metallic bismuth. On cooling the solution to room temperature bright orange crystals of the compound V (0.75 g) precipitated, decomposing at >160°C. Replacing benzene by hexane in the mother liquor gives an additional 0.13 g of this product. Total yield of the compound V is 0.98 g (62%). (Found: C, 27.00; H, 0.79; Bi, 32.94; mol. wt. 1340. $C_{28}H_{10}Bi_2F_{20}Ge_2$ calcd.: C, 26.08; H, 0.78; Bi, 32.41%; mol. wt. 1289.) After removal of the solvent and volatile products from the hexane moth solution, a viscous uncrystallizable and undistillable dark cherry liquid (0.81 g) remains.

Interaction of I with bromine

Br_2 (0.69 g, 4.28 mmol) in benzene (5 ml) was added in small portions to a solution of I (1.2 g, 1.43 mmol) in benzene (5 ml). During the reaction a residue of $BiBr_3$ (0.64 g, 100%) is formed. GLC analysis of the reaction mixture gave 0.29 g (94%) of ethyl bromide. After separating $BiBr_3$ and removing the solvent and volatile products in vacuo, 0.88 g (94%) of tris(pentafluorophenyl)germaniu bromide remains which was identified by means of GLC and IR spectroscopy.

Bromination of II and V were carried out similarly.

Interaction of II with HCl

0.03 g (0.82 mmol) of dry HCl gas was added to a solution of II (0.72 g, 0.52 mmol) in THF (5 ml) at room temperature. After 20 min the solvent was evaporated and the residue was extracted twice with hot hexane to form a yellow precipitate (m.p. 154—158°C) of $EtBiCl_2$ (0.14 g, 64%). (Found: C, 8.01 H, 1.71. $C_2H_5BiCl_2$ calcd.: C, 7.78; H, 1.63%.)

Evaporation of the solvent from the hexane extract gave 0.56 g (95%) of $(C_6F_5)_3GeH$ which was identified by GLC and IR spectroscopy.

Under similar conditions 0.51 g (100%) of tris(pentafluorophenyl)germane and 0.25 g (96%) of Et_2BiCl were obtained from 0.73 g of I and 0.03 g of HCl.

Reaction of V with HCl

To a dark red solution of V (1 g, 0.78 mmol) in 8 ml of THF, 0.12 g (3.29 mmol) of HCl was added. The resulting solution was stored for 3 d at room temperature. The colour of the solution turned light brown and bismuth (0.23 g 70%) was precipitated. After separation of bismuth and removal of THF, hexane was added to the residue. The crystals (0.04 g, 4%) of the initial compound V which precipitated were separated by decanting. GLC analysis of the mother liquor gave 0.69 g (95%) of $(C_6F_5)_2Ge(H)Cl$ *.

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* This compound was also obtained by another route:

$$(C_6F_5)_2GeBr_2 + Mg/Hg \xrightarrow[-70\div20^\circ C]{\text{ether}} [(C_6F_5)_2Ge]_n \xrightarrow[50^\circ C]{\text{HCl (THF)}} (C_6F_5)_2Ge(H)Cl$$

Boiling point of the product is 93—94°C/1 mmHg, m.p. 41—42°C, ν(Ge—H) 2165 cm^{-1}. (Found: C, 32.29; H, 0.31; F, 42.95. $C_{12}HClF_{10}Ge$ calcd.: C, 32.52; H, 0.23; F, 42.87%.)

Reaction of II with mercury

A mixture of II (1.01 g, 0.73 mmol), metallic mercury (25 g, 124.4 mmol) and THF (8 ml) was shaken for 6 d at room temperature. During this time the solution lost ist colour. The solution was decanted from excess mercury and Bi residue (0.04 g, 26%). The latter was separated from mercury in the form of $BiCl_3$, after the mixture of metals had been treated with hot concentrated hydrochloric acid. The solvent was evaporated from the organic layer, the residue washed with two portions (of 3 ml each) of hexane and recrystallized from a hexane/toluene mixture (2 : 1). 0.6 g (61%) of $[(C_6F_5)_3Ge]_2Hg$ was obtained, m.p. (mixed) 222—225°C (lit. [4] m.p. 228—231°C). IR spectrum is identical to that of the compound obtained as described in the literature [4].

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