Journal of Organometallic Chemistry, 110 (1976) 149—157
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

REACTIVITY OF THE GERMANIUM—GERMANIUM BOND IN 1,1,1-TRIETHYL-2,2,2-TRIS(PENTAFLUOROPHENYL)DIGERMANE

M.N. BOCHKAREV, N.S. VYAZANKIN, L.N. BOCHKAREV and G.A. RAZUVAEV *
Institute of Chemistry, U.S.S.R. Academy of Sciences, Gorky (U.S.S.R.)

(Received November 11th, 1975)

Summary

Digermane, $(C_6F_5)_3GeGeEt_3$ (I), and trigermane, $Et_3GeGe(C_6F_5)_2GeEt_3$ (II), are obtained from the reaction of Et_3GeNEt_2 with tris(pentafluorophenyl)germane and bis(pentafluorophenyl)germane, respectively. The germanium—germanium bonds of these compounds are cleaved on interaction with water, hydrogen chloride or copper(II), silver(I), gold(III) and bismuth(III) chlorides. Ethylmercuric chloride and $HgCl_2$ cleave the Ge—Ge bond of I to form the corresponding germylmercurials, i.e. $(C_6F_5)_3GeHgEt$ and $[(C_6F_5)_3Ge]_2Hg$. Elemental sulphur and selenium react with I by inserting a chalcogen atom into the Ge—Ge bond. Reactions proceed readily in THF or acetone solutions and very slowly in non-polar solvents. The mechanisms of the reactions are discussed.

Introduction

We have recently found that the germanium—germanium bond of hexakis(pentafluorophenyl)digermane possesses high reactivity [1]. Unlike hexaphenyldigermane, the perfluorinated analogue, $(C_6F_5)_3GeGe(C_6F_5)_3$, reacts with water, methanol, protic acids, mercury(II) chloride etc. under polar conditions via cleavage of the Ge—Ge bond. The enhanced reactivity of this digermane was explained by the high polarizability of the Ge—Ge bond under the influence of the polar solvent and the attacking reagent. Obviously, the reactivity of the organodigermanes depends strongly on the character of the organic groups bonded to the germanium atoms. These observations induced us to synthesize 1,1,1-triethyl-2,2,2-tris(pentafluorophenyl)digermane (I) and 1,1,1,3,3,3-hexaethyl-2,2-bis(pentafluorophenyl)trigermane (II) and to study their reactivity.

Results and discussion

Compounds I and II were obtained in good yields according to eq. 1. It is known that with common organogermanium hydrides, similar hydrogenolysis reactions of organogermanium—nitrogen compounds could not be realized [2].

$$(C_6F_5)_{4-n}GeH_n + n\ Et_3GeNEt_2 \xrightarrow{100^\circ C} (C_6F_5)_{4-n}Ge(GeEt_3)_n + n\ Et_2NH \quad (1)$$

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

In contrast, the hydrogenolytic fission of Sn—N bonds, by organotin and organogermanium hydrides, was recognized as an important method for the preparation of compounds with Sn—Sn and Sn—Ge bonds [2,3]. Attempts to prepare the digermane I, by reaction of $(C_6F_5)_3GeH$ with methoxytriethylgermane at 100° C (2 h), were unsuccessful.

Compounds I and II are colourless crystalline solids which may be distillated in vacuo without decomposition. The dipole moment of the digermane I in hexane, determined by a previously described method [4], is 6.2 D. Both compounds are slowly hydrolyzed in moist air to effect Ge—Ge bond scission. In polar solvents, such as acetone and THF, the hydrolysis proceeds much faster than in hexane or benzene. The compound II is less water sensitive than compound I. For example, hydrolysis of the digermane I in THF is complete at room temperature after 20 min, whereas in the case of compound II heating to 100° C is necessary. Treatment of compounds I and II with hydrogen chloride also causes scission of the germanium—germanium bonds (eq. 2).

$$\underset{(I,\ II)}{(C_6F_5)_nGe(GeEt_3)_{4-n}} + HX \rightarrow (C_6F_5)_nGeH_{4-n} + 4 - n\ Et_3GeX \quad (2)$$

$$(n = 2, 3; X = OH, Cl)$$

According to the data of gas-liquid chromatography a heterolitic cleavage of the trigermane II (eq. 2) proceeds, with formation of dihydride $(C_6F_5)_2GeH_2$ and compound Et_3GeX, together with a compound which is apparently the product of incomplete cleavage of Ge—Ge—Ge linkages. These results were confirmed by IR spectroscopy. The spectra of the product mixture of this reaction contains an absorption band at 2142 cm^{-1}, characteristic of the Ge—H bond in dihydride [5], and an absorption band at about 2070 cm^{-1}, which could be due to the Ge—H stretching mode in the intermediate hydride. We failed to isolate this compound from the reaction mixture by fractionation in vacuo or by crystallization, at low temperature, in hexane.

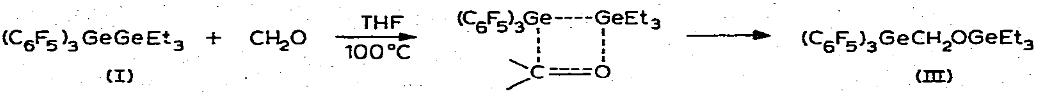
Although $(C_6F_5)_3GeGeEt_3$ is susceptible to hydrolytic decomposition, this compound does not react with such weakly acidic hydrocarbons as C_6F_5H ($pK_a = 23$) and $CHCl_3$ ($pK_a = 15$ [6]). Earlier we showed that hexakis(pentafluorophenyl)digermane is also inert towards reagents of this type [1].

Chalcogens react with $(C_6F_5)_3GeGeEt_3$, inserting into the Ge—Ge bond. In these reactions the activity of the chalcogens decreases in the order $S > Se > Te$. Thus, the sulphide derivative is formed at room temperature after 10—20 min, while reaction with selenium takes 4 h at 100° C (eq. 3). However, attempts to prepare the analogous telluride in a similar way failed.

$$I + 1/8\ X_8 \xrightarrow{THF} (C_6F_5)_3GeXGeEt_3 \quad (3)$$

$$(X = S, Se)$$

In the reaction of the digermane I with formaldehyde at 100° C, the main product is triethyl[tris(pentafluorophenyl)germylmethoxy]germane (III). It is



(I) (III) (4)

very likely that a four-centre process is operative (eq. 4). The structure of adduct III is confirmed by chemical methods. Thus, hydrolysis or hydrochlorination of III gives the carbinol $(C_6F_5)_3GeCH_2OH$ by scission of the Ge—O bond (eq. 5).

$$\underset{\text{(III)}}{(C_6F_5)_3GeCH_2OGeEt_3} + HX \xrightarrow[20^\circ C]{THF} (C_6F_5)_3GeCH_2OH + Et_3GeX \quad (5)$$

(X = OH, Cl)

$(C_6F_5)_3GeCH_2OH$ is isolated as an colourless waxy solid.

Earlier we showed [7] that unsymmetrical distannane, $(C_6F_5)_3SnSnEt_3$, reacts in benzene solution at 100°C with $(C_6F_5)_3SnBr$ to form hexakis(pentafluorophenyl)distannane and Et_3SnBr. A similar reaction of germanium analogues, in benzene under comparable conditions, does not occur. However, in THF more than 60% of $(C_6F_5)_6Ge_2$ and Et_3GeBr are formed at room temperature (eq. 6).

$$I + (C_6F_5)_3GeBr \xrightarrow[20^\circ C,\ 30\ min]{THF} (C_6F_5)_3GeGe(C_6F_5)_3 + Et_3GeBr \quad (6)$$

It has also been shown that triethyltin chloride reacts with the digermane I to give $(C_6F_5)_3GeSnEt_3$ and triethylgermanium chloride, but the compound I has not been cleaved by $(C_6F_5)_3SnBr$ or $(C_6F_5)_3SiBr$, even at 100°C in benzene or THF solution.

It may be expected that the digermane I can be used for the synthesis of compounds with germanium—metal bonds. However, reaction of I with ethyllithium in diethyl ether, or with lithium amalgam in THF, yields a complex mixture of products in which no $(C_6F_5)_3GeLi$ is detected. We noted that earlier attempts to prepare $(C_6F_5)_3GeLi$ or $(C_6F_5)_3SiLi$ were also unsuccessful [8,9]. In contrast, mercury(II) chloride and ethylmercuric chloride react with the digermane I to give germylmercurial analogues in high yield (eq. 7, 8). It is known that

$$2\,I + HgCl_2 \xrightarrow[20^\circ C,\ 3\ h]{THF} [(C_6F_5)_2Ge]_2Hg + 2\ Et_3GeCl \quad (7)$$

$$I + EtHgCl \xrightarrow[20^\circ C,\ 15\ min]{THF} (C_6F_5)_3GeHgEt + Et_3GeCl \quad (8)$$

$(C_6F_5)_3GeGe(C_6F_5)_3$ reacts with ethylmercuric chloride analogously, to give $(C_6F_5)_3GeHgEt$ and $(C_6F_5)_3GeCl$, while its reaction with mercury(II) chloride affords only Hg_2Cl_2 and $(C_6F_5)_3GeCl$ [1].

In the reactions with $CuCl_2$, AgCl, $AuCl_3$ and $BiCl_3$, the digermane I shows distinct reduction properties (eq. 9—11). I does not react with Cu_2Cl_2, $ZnCl_2$ and $CdBr_2$ under comparable conditions.

The formation of tris(pentafluorophenyl)germane (50—60% yield) in reactions 9 and 10 is due to the reaction of generated $(C_6F_5)_3Ge^\bullet$ radicals with the solvent. Since the formation of these radicals cannot be detected by ESR methods we carried out reaction 9 in the presence of 2,4,6-tri-t-butylphenol. In this case a considerable concentration of 2,4,6-tri-t-butylphenoxyl radicals (triplet 1/2/1, $a_n^M = 1.8$ e [10]) was detected in the reaction mixture. These are formed in accordance with eq. 12. It should be noted that the intensity of the ESR signal

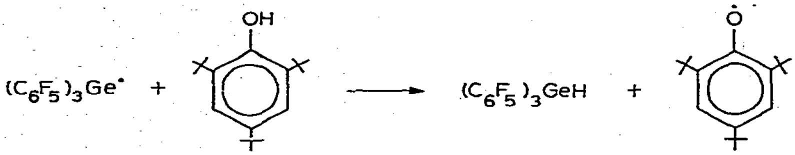
$$2\,I + 2\,CuCl_2 \xrightarrow[20-50^\circ C]{THF} 2\,(C_6F_5)_3GeH + 2\,Et_3GeCl + Cu_2Cl_2 \quad (9)$$

$$n\,I + MCl_n \xrightarrow[20-100^\circ C]{THF} n\,(C_6F_5)_3GeH + n\,Et_3GeCl + M \quad (10)$$

$(M = Ag, n = 1; M = Au, n = 3)$

$$3\,I + 2\,BiCl_3 \xrightarrow[100^\circ C,\ 1\ h]{THF} 3\,(C_6F_5)_3GeCl + 3\,Et_3GeCl + 2\,Bi \quad (11)$$

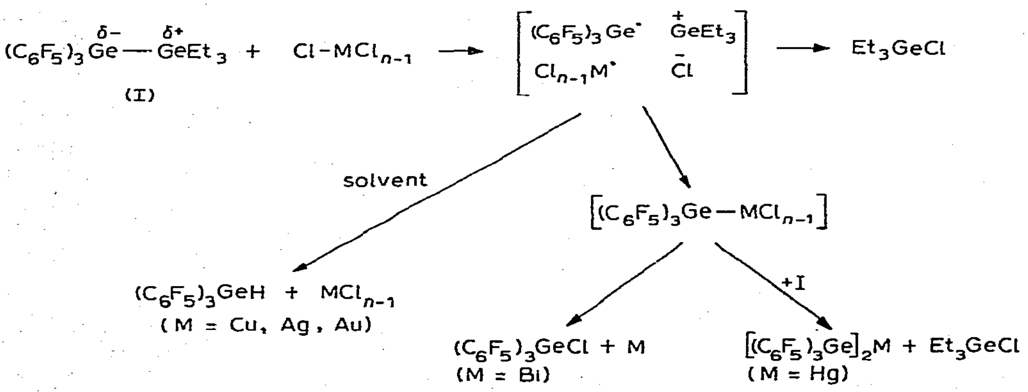
passes through a maximum, rapidly decreases and eventually the signal disappears.



(12)

It is natural to assume that compound I reacts with metal chlorides via a one-electron transfer (Scheme 1). The resulting radical $(C_6F_5)_3Ge^\cdot$ then abstracts

SCHEME 1



hydrogen from a neighbouring molecule to give tris(pentafluorophenyl)germane or recombines with the $\cdot MCl_{n-1}$ radical, forming stable compounds (e.g. $[(C_6F_5)_3Ge]_2Hg$). Reaction of I with $BiCl_3$ gives the intermediate $(C_6F_5)_3GeBiCl_2$, which is converted to $(C_6F_5)_3GeCl$ and metallic bismuth by thermal fragmentation.

The role of the electron-donor solvent, which is not shown in Scheme 1, is in increasing the electron density in the Ge—Ge bond, and therefore in facilitating electron transfer. Scheme 1 is in agreement with that proposed earlier for oxidation of distannanes, $R_3SnSnR'_3$, by iron(III) complexes [11].

Comparison of the data obtained with the values of the normal electrode potentials for the salts used, shows that I in THF solution enters into redox reactions with salts which have $E_0 \geqslant +0.21$ V. Weaker oxidizing agents do not react with I under the given conditions. Very strong reducing agents interact with the digermane I but in this case, as has been noted above, together with the Ge—Ge bond, the fluorinated benzene rings are attacked.

IR spectra of the digermane I and trigermane II exhibit a number of absorption bands characteristic for Et_3Ge fragments [12] and for C_6F_5 groups bonded to the germanium atom [13]. The presence of the Ge—O—R fragment in $(C_6F_5)_3GeCH_2OGeEt_3$ is confirmed by the existence of absorption bands at about 580 and 1080 cm^{-1}. The presence of the hydroxyl group in carbinol $(C_6F_5)_3GeCH_2OH$ results in the appearance of an absorption band with a frequency of about 3430 cm^{-1}.

Experimental

All reactions were carried out in evacuated sealed ampoules. GLC analyses of products were carried out on a "Tsvet 104" chromatograph equipped with a catarometer detector; helium was used as the carrier gas. The columns used were: 100 × 0.4 cm packed with Apiezon L (20%) on Chromosorb "W" and 100 × 0.4 cm packed with CX-80 modified with trimethylsilicon chloride. IR spectra were recorded on a UR-20 instrument. The dipole moment was determined by use of a "Dipol" instrument.

Tris(pentafluorophenyl)germane and bis(pentafluorophenyl)germane were prepared by a previously described method [5].

1,1,1-Triethyl-2,2,2-tris(pentafluorophenyl)digermane (I)

A mixture of $(C_6F_5)_3GeH$ (4.40 g, 7.7 mmol) and triethylgermanium diethyl amide (2.01 g, 8.7 mmol) in hexane (25 ml) was heated for 1 h at 100°C and the resulting solution stored at —10°C for 30 h. The white crystalline solid obtained (4.10 g, 73%) was thrice recrystallized from hexane to give the desired product; m.p. 98—102°C; b.p. 144—151°C/1.5 mm Hg. (Found: C, 39.20; H, 2.20; F, 38.66. $C_{24}H_{15}F_{15}Ge_2$ calcd.: C, 39.30; H, 2.21; F, 38.85%.) The volatile products were isolated from the mother solution by vacuum distillation. 0.51 g (91%) of diethylamine was detected (GLC).

1,1,1,3,3,3-Hexaethyl-2,2-bis(pentafluorophenyl)trigermane (II)

A mixture of bis(pentafluorophenyl)germane (3.18 g, 7.8 mmol) and triethylgermanium diethyl amide (3.61 g, 15.6 mmol) was heated for 1 h at 100°C. The diethyl amine formed (1.06 g, 93%) was isolated from the reaction mixture by vacuum distillation. After fractionating the residue, the trigermane II (3.75 g, 66%) was obtained; b.p. 164—166°C/1.5 mm Hg. The colourless viscous oil crystallized upon standing; m.p. 41—44°C. (Found: C, 40.05; H, 4.14; F, 26.21. $C_{24}H_{30}F_{10}Ge_3$ calcd.: C, 39.69; H, 4.16; F, 26.16%.)

Hydrolysis of digermane I

To a solution of I (1.50 g, 2.0 mmol) in THF (6 ml), at room temperature, water (0.63 g, 34.8 mmol) was added. Samples withdrawn after 15 min, analyzed by GLC, showed the absence of the starting product. The reaction mixture was heated at 80°C for 5 min. After cooling, GLC analysis of the mixture gave hexaethyldigermoxane (0.30 g, 88%) and $(C_6F_5)_3GeH$ (0.96 g, 82%).

Hydrolysis of trigermane II

When an mixture of II (1.61 g, 2.2 mmol) and water (0.63 g, 34.8 mmol) in THF (8 ml) was heated for 1 h at 100° C new IR absorption bands at 2142 cm^{-1} [ν(Ge—H) of $(C_6F_5)_2GeH_2$ (see [5])] and 2074 cm^{-1} [ν(Ge—Ge—H) of $Et_3GeGeH(C_6F_5)_2$] appeared. The formation of bis(pentafluorophenyl)germane, together with $Et_3GeGeH(C_6F_5)_2$ and hexaethyldigermoxane, was also detected by GLC. After heating the reaction mixture at 100° C for an additional hour, the Ge—H absorption band at 2070 cm^{-1} disappeared from the spectrum and only germanium dihydride (0.90 g, 100%) and digermoxane (0.71 g, 96%) were detected by GLC.

Reaction of I with HCl

A solution of hydrogen chloride (0.10 g, 2.8 mmol) in THF (8 ml) was added to the digermane I (1.04 g, 1.4 mmol). The mixture was kept at 20° C for 20 min and the volatile products were distilled in vacuo. The residue was recrystallized from hexane to give $(C_6F_5)_3GeH$ (0.82 g, 100%); m.p. (mixed) 129—132° C (the authentic specimen was obtained as preveiously described [13]). GLC analysis of the volatiles revealed the presence of triethylgermanium chloride (0.24 g).

Reaction of II with HCl

A mixture of the trigermane II (1.53 g, 2.1 mmol) and HCl (0.31 g, 8.6 mmol) in THF (10 ml) was heated at 50° C for 30 min. GLC analysis of the reaction mixture revealed the presence of the initial compound II, triethylgermanium chloride, the dihydride $(C_6F_5)_2GeH_2$ and a considerable amount of the expected digermane $Et_3GeGeH(C_6F_5)_2$. After heating the mixture at 50° C for an additional 1.5 h only $(C_6F_5)_2GeH_2$ (0.75 g, 87%) and Et_3GeCl (0.76 g, 92%) were detected by GLC.

Reaction of II with methanol

The trigermane II (2.44 g, 3.4 mmol) and methanol (0.17 g, 5.3 mmol) in THF (5 ml) were heated for 9 h at 50° C. According to the GLC data, the mixture contains Et_3GeOMe, bis(pentafluorophenyl)germane, the expected digermane $Et_3GeGeH(C_6F_5)_2$ as well as 15% of the initial trigermane II. Additional heating does not change the ratio of these components. After removing the solvent and volatile products by vacuum distillation, 1.72 g of a viscous liquid was obtained which contained (according to the GLC data) the initial trigermane II (0.16 g), $(C_6F_5)_2GeH_2$ (0.22 g) and the expected digermane $Et_3GeGeH(C_6F_5)_2$ (0.96 g). The IR spectrum of the mixture was identical with that of the reaction mixture obtained after heating II for 1 h with H_2O at 100° C. An attempt to separate the components of the reaction mixture by vacuum fractionation was unsuccessful.

Triethylmethoxygermane (0.04 g) was found in the volatile products (GLC).

Reaction of I with sulphur

A mixture of I (1.50 g, 2.0 mmol) and sulphur (0.07 g, 2.2 mmol) in THF (12 ml) was stirred for 10 min at 20° C. Distillation of the mixture gave $(C_6F_5)_3GeSGeEt_3$ (1.44 g, 92%), b.p. 134—136° C/1 mm Hg; n_D^{20} 1.5199 (lit. [14] b.p. 133—134° C/1 mm Hg; n_D^{20} 1.5204).

Under more vigorous conditions (100° C, 4 h) the digermane I reacts with selenium. Yield of $(C_6F_5)_3GeSeGeEt_3$ was 97%; b.p. 164—165° C/1 mm Hg; n_D^{20} 1.5344 (lit. [14] b.p. 164—166° C/1 mm Hg; n_D^{20} 1.5338).

Triethyl[tris(pentafluorophenyl)germylmethoxy]germane (III)

A solution of the digermane I (2.00 g, 2.7 mmol) in THF (7 ml) was placed in a 100 ml evacuated ampoule. Gaseous formaldehyde was condensed, by cooling with liquid nitrogen, into the ampoule before sealing and then the contents were heated at 100° C for 2 h. After the THF had been distilled off, the residue was vacuum distilled to give $(C_6F_5)_3GeCH_2OGeEt_3$ (III) (0.93 g, 45%); b.p. 149—152° C/1.5 mm Hg; n_D^{20} 1.4892. (Found: C, 39.09; H, 2.31; F, 37.37. $C_{25}H_{17}F_{15}Ge_2O$ calcd.: C, 39.33; H, 2.24; F, 37.32%.)

Reaction of III with HCl

A solution of III (1.60 g, 2.1 mmol) and hydrogen chloride (0.12 g, 3.3 mmol) in THF (3 ml) was allowed to stand at room temperature for 15 min. The disappearance of III in the reaction mixture was detected by GLC. Trap-to-trap distillation of the volatiles, at 1 mm Hg, gave a clear distillate which was shown to contain Et_3GeCl (0.21 g, 51%), by GLC. The residue in the trap-to-trap distillation vessel was dissolved in hexane, and the resulting solution stored at —30° C. The colourless waxy solid obtained was recrystallized from hexane at the same temperature; yield of $(C_6F_5)_3GeCH_2OH$ was 0.85 g (67%). The compound passes into the liquid state in the temperature range 18—32° C (Found: C, 37.92; H, 0.93; F, 46.96. $C_{19}H_3F_{15}GeO$ calcd.: C, 37.73; H, 0.50, F, 47.12%.)

Reaction of I with tris(pentafluorophenyl)germanium bromide

To a solution of I (0.56 g, 0.8 mmol) in THF (2 ml) was added, at room temperature, a solution of $(C_6F_5)_3GeBr$ (0.5 g, 0.8 mmol) in THF (2 ml). After 3—5 min the reaction was complete and hexakis(pentafluorophenyl)digermane precipitated. The liquid layer was decanted from the digermane which itself was sublimed at 210—230° C/1 × 10^{-2} mm Hg. The yield was 0.58 g (66%); m.p. (mixed) 312—318° C. GLC analysis of the volatile products showed Et_3GeBr (0.14 g, 78%) to be present.

Reaction of I with triethyltin chloride

A solution of the digermane I (1.38 g, 1.9 mmol) and Et_3SnCl (0.46 g, 1.9 mmol) in THF (10 ml) was kept at room temperature for 15 min. The absence of I in the reaction mixture was demonstrated by GLC. The volatile products were removed in vacuo. The residue was dissolved in hexane and the resulting solution was stored at —85° C for 6 h. $(C_6F_5)_3GeSnEt_3$ (0.62 g, 42%) was obtained; m.p. (mixed) 71—74° C (the authentic specimen was obtained as previously described [5]). GLC analysis of the volatile products showed that triethylgermanium chloride (0.36 g, 100%) was present.

Reaction of I with ethylmercuric chloride

A solution of the digermane I (1.38 g, 1.9 mmol) and ethylmercuric chloride (0.57 g, 2.1 mmol) in THF (10 ml) was stored at room temperature for 20 h and then heated at 50° C for 15 min. The volatile products were removed in vacuo.

The residue was recrystallized twice from hexane. $(C_6F_5)_3GeHgEt$ (1.17 g, 78%) was obtained; m.p. (mixed) 118—121°C (lit. [13] m.p. 118—121°C). Et_3GeCl (0.30 g, 82%) in the volatiles was detected by GLC.

Reaction of I with mercury(II) chloride

A mixture of the digermane I (1.50 g, 2.0 mmol) and mercury(II) chloride (0.30 g, 1.1 mmol) in THF (10 ml) was stirred at 20°C for 3 h and then at 95°C for 15 min. Metallic mercury (0.06 g, 27%) was precipitated and the organic layer decanted from the mercury. After removal of the solvent and volatile products, the crystalline residue was washed with hexane and dried in vacuo to afford $[(C_6F_5)_3Ge]_2Hg$ (0.99 g, 72%); m.p. 218—227°C. Recrystallization from toluene gave a sample of m.p. (mixed) 229—231°C. A further quantity of triethylgermanium chloride (0.31,g, 78%) was found by GLC in the volatile products.

Reaction of I with copper(II) chloride

To a freshly prepared copper(II) chloride (0.27 g, 2.0 mmol) a solution of I (1.49 g, 2.0 mmol) in THF (15 ml) was added. The mixture was kept at room temperature for 30 min, after which time the characteristic brown colour of the copper(II) salt had disappeared. The reaction occurred with the precipitation of Cu_2Cl_2. The mixture was heated at 50°C for 30 min, and the organic layer was decanted from Cu_2Cl_2 (0.21 g, 100%). GLC analysis of the organic layer showed the presence of three major and three minor components. The former were triethylgermanium chloride (0.21 g, 53%), tris(pentafluorophenyl)germane (0.58 g, 50%) and hexakis(pentafluorophenyl)digermane (0.24 g, 20%).

Reaction of I with silver(I) chloride

A mixture of I (1.19 g, 1.6 mmol) and silver(I) chloride (20 g, 139.6 mmol) in THF (15 ml) was heated in darkness at 100°C for 3 h, with periodic shaking. The metallic silver began to precipitate out almost immediately. The organic layer was decanted from the metallic silver (0.20 g, 113%) and silver(I) chloride. GLC analysis of the organic layer showed the presence of Et_3GeCl (0.24 g, 76%), $(C_6F_5)_3GeH$ (0.52 g, 56%) and the initial digermane I (<1%).

Reaction of I with gold(III) chloride

A mixture of I (0.50 g, 0.7 mmol), gold(III) chloride (0.06 g, 0.2 mmol) in THF (3 ml) was heated at 100°C for 45 min. The metallic gold began to precipitate almost immediately. The organic layer was decanted from gold (0.04 g, 100%). GLC analysis of the organic layer showed the presence of triethylgermanium chloride (0.08 g, 60%) and $(C_6F_5)_3GeH$ (0.18 g, 46%).

Reaction of I with bismuth(III) chloride

The solution of digermane I (1.49 g, 2.0 mmol) and $BiCl_3$ (0.66 g, 2.1 mmol) in THF (12 ml) was heated for 1 h at 100°C. The organic layer was decanted from metallic bismuth (0.36 g, 82%). The volatiles were distilled in vacuo, into a trap cooled by liquid nitrogen. In the condensate Et_3GeCl (0.36 g, 91%) was detected by GLC. The residue in the trap-to-trap distillation vessel was recrystallized from hexane. $(C_6F_5)_3GeCl$ (1.02 g, 83%) was obtained; m.p. 103—105°C. No depression of the m.p. was caused by mixing with the pure substance.

References

1 M.N. Bochkarev, G.A. Razuvaev and N.S. Vyazankin, Izv. Akad. Nauk SSSR, Ser. Khim., (1975) 1820; M.N. Bochkarev, G.A. Razuvaev, N.S. Vyazankin and O.Yu. Semenov, J. Organometal. Chem., 74 (1974) C4.

2 H.M.J.C. Creemers and J.G. Noltes, J. Organometal. Chem., 7 (1967) 237.

3 H.M.J.C. Creemers, Hydrostannolysis, a general method for establishing tin—metal Bonds, Schotanus and Jens, Utrecht 1967.

4 K. Higasi, Bull. Inst. Phys. Chem. Res., 22 (1943) 85.

5 M.N. Bochkarev, L.P. Maiorova, S.P. Korneva, L.N. Bochkarev and N.S. Vyazankin, J. Organometal. Chem., 73 (1974) 229.

6 K.P. Butin, A.N. Kashin, I.P. Beletskaya, L.S. German and V.R. Polishchuk, J. Organometal. Chem., 57 (1973) 111.

7 M.N. Bochkarev, S.P. Korneva, L.P. Maiorova, V.A. Kuznetsov and N.S. Vyazankin, Zh. Obshch. Khim., 44 (1974) 308.

8 D.E. Fenton, A.G. Massey and D.S. Urch, J. Organometal. Chem., 6 (1966) 352.

9 C. Tamborski, E.J. Soloski and S.M. Dec, J. Organometal. Chem., 4 (1965) 446.

10 V.D. Pokhodenko, Phenoxyl Radicals, "Naukova Dumka", Kiev, 1969.

11 A. Pesolo, J. Organometal. Chem., 74 (1974) 59.

12 A.N. Egorochkin, N.S. Vyazankin, M.N. Bochkarev and S.Ya. Khorshev, Zh. Obshch. Khim., 37 (1967) 1165.

13 M.N. Bochkarev, L.P. Maiorova and N.S. Vyazankin, J. Organometal. Chem., 55 (1973) 89.

14 M.N. Bochkarev, L.P. Maiorova, N.S. Vyazankin and G.A. Razuvaev, J. Organometal. Chem. 82 (1974) 65.