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NEW ROUTES TO PENTAFLUOROPHENYL DERIVATIVES WITH GERMANIUM—CHALCOGEN BONDS

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Summary

Tris(pentafluorophenyl)germanethiol, $(C_6F_5)_3GeSH$ (Ia), was obtained in good yield by heating the tris(pentafluorophenyl)germane with elemental sulphur or by the exchange between Et_3GeSH and $(C_6F_5)_3GeBr$. The reaction between sulphur and $(C_6F_5)_2GeH_2$ or $C_6F_5GeH_3$ gives heterocyclic products with chains of alternating germanium and sulphur atoms in the cycles. The compounds $[(C_6F_5)_3Ge]_2X$ (X = S, Se) were prepared by exchange reaction of $(Et_3Ge)_2X$ with tris(pentafluorophenyl)germanium bromide and by reaction of chalcogens (S_8, Se_8) with hexakis(pentafluorophenyl)digermane. Ia reacts with diethylmercury affording $(C_6F_5)_3GeSHgEt$. Insertion of elemental sulphur into the Ge—Hg bond of bis[tris(pentafluorophenyl)germyl]mercury led to the thermally stable $(C_6F_5)_3GeSHgGe(C_6F_5)_3$.

Introduction

Although the chemistry of pentafluorophenyl organometallics is now quite extensive (for reviews, see refs. 1 and 2), the available synthetic routes for preparation of fluoroaromatic derivatives containing germanium—chalcogen bonds are relatively few. Earlier we found [3-7] that elemental sulphur, selenium and tellurium react with trialkylgermanes, R_3GeH, at high temperatures with insertion of a chalcogen atom into the germanium—hydrogen bond. The R_3GeXH compounds so obtained (X = S, Se, Te) are highly reactive and thus are useful for preparative work, especially for the synthesis of various organogermanium derivatives with germanium—chalcogen bonds.

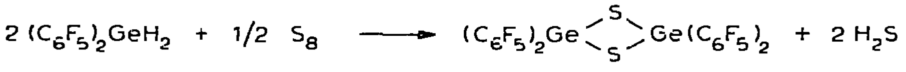
The insertion reaction of chalcogens into M—H bond of organometallics (M = Si, Ge, Sn) is probably general. For example, the compounds Et_3SiSH and Et_3SiSeH [6, 7], Ph_3SiSH [7-9] and $(p\text{-}MeC_6H_4)_3SiSH$ [10] have been obtained in a similar manner. In the present work this reaction was employed along with other methods for the syntheses of pentafluorophenyl derivatives with germanium—chalcogen bonds.

Results and discussion

In continuation of our research [11, 12] on reactivity of pentafluorophenylgermanes $(C_6F_5)_nGeH_{4-n}$ (n = 1-3), we have shown that tris(pentafluorophenyl)germane reacts with sulphur at 135° to give tris(pentafluorophenyl)germanethiol (Ia) (see eqn. 1 and Table 1).

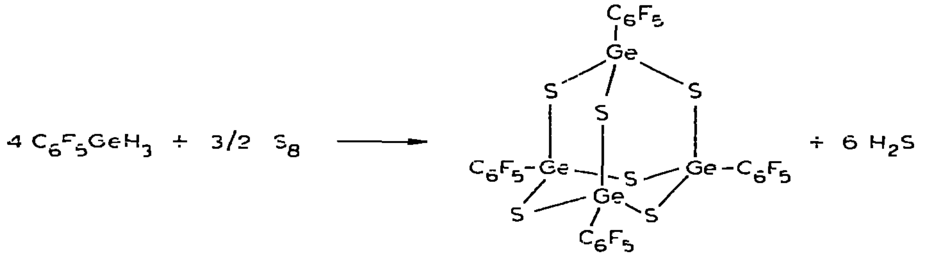
$$(C_6F_5)_3GeH + 1/8\ S_8 \rightarrow \underset{(Ia)}{(C_6F_5)_3GeSH} \qquad (1)$$

In contrast, the action of sulphur on di- and tri-hydrides leads probably, in the first instance, to the corresponding intermediates such as $(C_6F_5)_2Ge(SH)_2$ and $C_6F_5Ge(SH)_3$, which cyclise to form heterocyclic compounds II and III (cf. ref. 13) with evolution of hydrogen sulphide (eqns. 2 and 3).



(II)

(2)



(III)

(3)

The structures of 1,3-bis(pentafluorophenyl)-cyclo-1,3-digerma-2,4-dithiane, II and the adamantane-like compound III were proposed on the basis of analytical and molecular weight data. Moreover the formation of heterocyclic structures of type II has been observed in reactions of dialkoxydibutylgermanes with hydrogen sulphide [13]. This is also in accord with the closely-related reactio of sulphur with $C_6H_5SiH_3$, in the course of which a compound with an adamantan structure similar to III is formed [14].

Compounds II and III are highly fusible, colourless, stable in air, crystalline compounds (Table 1).

We note that attempts to carry out the reactions similar to eqns. 1-3 between elemental selenium and compounds of the series $(C_6F_5)_nGeH_{4-n}$ failed. No reactio was observed below 200°, while the starting germanes decomposed under the more vigorous conditions.

Earlier we showed [15] that the compounds $[(C_6F_5)_3Sn]_2X$ (X = S, Se, Te) are obtained in high yield in exchange reactions of $(C_6F_5)_3SnBr$ with $(Et_3Ge)_2X$. Similar reactions occur between tris(pentafluorophenyl)germanium bromide and triethylgermanethiol, bis(triethylgermyl)sulphide and related compounds (eqns.

4 and 5). The exchange of $(C_6F_5)_2GeBr_2$ with triethylgermanethiol is accompanied

$$(C_6F_5)_3GeBr + Et_3GeXH \xrightarrow{150^\circ} \underset{\text{(I)}}{(C_6F_5)_3GeXH} + Et_3GeBr \qquad (4)$$

(a, X = S; b, X = Se)

$$\begin{tikzcd}[column sep=small] (C_6F_5)_3GeBr + (Et_3Ge)_2X \arrow[r, "150^\circ"] & \underset{\text{(IV)}}{(C_6F_5)_3GeXGeEt_3} + Et_3GeBr \arrow[d, "+ (C_6F_5)_3GeBr"'] \\ & \underset{\text{(V)}}{[(C_6F_5)_3Ge]_2X} + Et_3GeBr \end{tikzcd} \qquad (5)$$

(a, X = S; b, X = Se)

by a condensation reaction owing to the high lability of the $=Ge(SH)_2$ grouping and as a result compound II was obtained in 40% yield instead of the expected bis(pentafluorophenyl)germanedithiol, $(C_6F_5)_2Ge(SH)_2$. Other reaction products are triethylgermanium bromide and hydrogen sulphide.

Reaction 5 may proceed selectively with formation of asymmetric compounds IVa and IVb or bis[tris(pentafluorophenyl)germyl]chalcogenides Va and Vb. The course of reaction is determined mainly by the ratio of the starting reagents. Compounds Va and Vb may also be obtained in satisfactory yields by reaction of sulphur or selenium with hexakis(pentafluorophenyl)digermane in tetrahydrofuran. Chalcogen insertion into the Ge—Ge bond occurs under unexpectedly mild conditions (60-100°). Other reactions demonstrating the enhanced reactivity of the Ge—Ge bond in $(C_6F_5)_3GeGe(C_6F_5)_3$ have been described [16].

It is interesting to note that in compounds $(C_6F_5)_3Ge{-}X{-}GeEt_3$ (IVa and IVb) the $X{-}GeEt_3$ bond is more active than the $X{-}Ge(C_6F_5)_3$ bond. In accord with this the exchange reactions of $(C_6F_5)_3SnBr$ with IVa and IVb gave pentafluorophenyl derivatives $(C_6F_5)_3GeXSn(C_6F_5)_3$ in 60% yield (eqn. 6).

$$\underset{\text{(IV)}}{(C_6F_5)_3GeXGeEt_3} + (C_6F_5)_3SnBr \rightarrow \underset{\text{(VI)}}{(C_6F_5)_3GeXSn(C_6F_5)_3} + Et_3GeBr \qquad (6)$$

(a, X = S; b, X = Se)

Finally we have found that germanethiol Ia reacts under mild conditions with an equimolar amount of diethylmercury giving compounds with Ge—S—Hg grouping (eqn. 7). Under these conditions the use of germanethiol excess does

$$(C_6F_5)_3GeSH + Et_2Hg \xrightarrow{20\text{-}50^\circ} \underset{\text{(VII)}}{(C_6F_5)_3GeSHgEt} + C_2H_6 \qquad (7)$$

not release the second mole of ethane. VII, analogously to previously-prepared compounds $Et_3GeXHgEt$ (X = S, Se) [17] decomposes slowly at room temperature with formation of metallic mercury.

A pentafluorophenyl derivative with the Ge—S—Hg—Ge grouping was prepared by reaction of an equimolar ratio of bis[tris(pentafluorophenyl)germyl]-mercury with elemental sulphur in THF (eqn. 8). Unlike the ethyl analogue [18] this compound is highly fusible (m.p. 169-173°).

$$[(C_6F_5)_3Ge]_2Hg + 1/8\ S_8 \left[\xrightarrow[50^\circ]{THF}\right] \underset{(VIII)}{(C_6F_5)_3GeSHgGe(C_6F_5)_3} \qquad (8)$$

The IR spectra of all compounds prepared (see Table 1) exhibit a number of bands specific of the C_6F_5Ge fragments [11]. Moreover, the spectra of the S derivatives (Ia, II, III, IVa, Va, VIa, VII and VIII) contain absorption bands at 415-440 cm^{-1} which may be due to the stretching modes of Ge—S bonds. The spectra of IVa and IVb also contain frequencies corresponding to the Et_3Ge moiety [19]. The S—H Ia and Se—H Ib stretching modes have their frequencies at 2600 and 2430 cm^{-1} respectively.

TABLE 1

PROPERTIES OF THE PENTAFLUOROPHENYLGERMANIUM CHALCOGEN COMPOUNDS

No.	Compound	Yield (%)	M.p. (°C)	Analysis found (calcd.) (%) C	H	F	Mol. wt found (calcd.)
Ia	$(C_6F_5)_3GeSH$	76.8[a]	105-107	35.72 (35.63)	—	46 96 (46.96)	583[b] (607)
Ib	$(C_6F_5)_3GeSeH$	73.2	102-105	33.16 (33 07)	—	43.39 (43.59)	—
II	$[(C_6F_5)_2GeS]_2$	78.6[c]	196-198	—	—	43.34 (43.30)	890[d] (878)
III	$(C_6F_5)_4Ge_4S_6$	79.6	263-265	25.37 (25.05)	—	33.13 (33.01)	1203[d] (1151)
IVa	$(C_6F_5)_3GeSGeEt_3$	74.2	[e]	37.84 (37.65)	1.93 (1.97)	37.24 (37.22)	—
IVb	$(C_6F_5)_3GeSeGeEt_3$	65.6	[f]	36.00 (35.48)	1.82 (1.86)	35.06 (35.07)	—
Va	$[(C_6F_5)_3Ge]_2S$	76.8[g]	165-169	36 66 (36.66)	—	48.36 (48.32)	—
Vb	$[(C_6F_5)_3Ge]_2Se$	43 8[g]	158-161	35 58 (35.26)	—	46.54 (46.47)	—
VIa	$(C_6F_5)_3GeSSn(C_6F_5)_3$	60.5	145-147	35.53 (35.28)	—	46.64 (46.50)	—
VIb	$(C_6F_5)_3GeSeSn(C_6F_5)_3$	60.3	135-137	33.99 (33.98)	—	44.92 (44.79)	—
VII	$(C_6F_5)_3GeSHgEt$	61.2	105-108	—	—	34.35 (34.11)	—
VIII	$(C_6F_5)_3GeSHgGe(C_6F_5)_3$	63.5	169-173	31.32 (31.33)	—	41.58 (41.29)	—

[a] Yield in reaction 4. [b] Mol. wt. was determined by cryoscopy in benzene. [c] Yield in reaction 2. [d] Mol. wt. was determined by K. Rask method in camphor. [e] B.p. 133-134°/1 mmHg, n_D^{20} 1.5204. [f] B.p. 164-166°/1 mm Hg, n_D^{20} 1.5338. [g] Yield in reaction 5.

Experimental

All reactions were carried out in evacuated sealed ampoules or under argon. Identification and analysis of the gaseous and volatile products were carried out by GLC on a Tsvet-1 chromatograph with a catarometer detector and helium as the carrier gas. The IR spectra were recorded on a UR-20 spectrophotometer.

Tris(pentafluorophenyl)germanethiol (Ia)

(a). 3.62 g (6.28 mmol) of $(C_6F_5)_3GeH$ [12] and 0.21 g (6.55 mmol) of sulphur were heated at 135° for 2.5 h and at 150° for 1.5 h. The reaction products were recrystallized from hexane (−78°). 2.21 g (58.0%) of Ia was obtained, m.p. 100-105°. Mixed melting with Ia prepared by reaction 4 showed no depression.

(b). A mixture of 5.07 g (7.75 mmol) of $(C_6F_5)_3GeBr$ and 1.49 g (7.73 mmol) of triethylgermanethiol was heated at 150° for 18 h and the volatile products were removed by condensation in vacuo. GLC analysis of the condensate revealed 1.48 g (79.9%) of triethylgermanium bromide. Recrystallization of the residue from hexane afforded 3.60 g (76.8%) of Ia.

Compound Ib was obtained analogously by reaction 4 (see Table 1).

1,3-bis(pentafluorophenyl)-cyclo-1,3-digerma-2,4-dithiane(II)

(a). A mixture of 1.99 g (4.87 mmol) of bis(pentafluorophenyl)germane [12] and 0.31 g (9.67 mmol) of sulphur was heated at 170° for 30 min and at 190° for 30 min. 82 ml (75.2%) of hydrogen sulphide was evolved. The crystalline solid produced was recrystallized twice from hexane. 1.68 g (78.7%) of II was obtained.

(b). 3.19 g (5.63 mmol) of bis(pentafluorophenyl)germanium dibromide and 2.04 g (10.58 mmol) of Et_3GeSH were heated at 150° for 16 h. 57 ml (48.3%) of hydrogen sulphide was evolved. The solid was recrystallized twice from hexane. Yield of II was 1.86 g (40.1%). GLC analysis of the mother liquid gave 1.81 g (71.4%) of triethylgermanium bromide.

Reaction of pentafluorophenylgermane with sulphur

2.63 g (10.84 mmol) of $C_6F_5GeH_3$ [12] and 1.04 g (32.44 mmol) of sulphur were placed in an ampoule filled with argon and connected to a gas burette. The mixture was heated at 150° for 30 min and at 170° for 30 min. 245 ml (100%) of hydrogen sulphide was evolved. The resultant crystalline solid was recrystallized twice from toluene/hexane (1/3). Yield of compound III was 2.48 g (79.6%).

Triethylgermyl[tris(pentafluorophenyl)germyl] selenide (IVb)

5.47 g (8.37 mmol) of tris(pentafluorophenyl)germanium bromide and 3.55 g (8.42 mmol) of $(Et_3Ge)_2Se$ were heated at 150° for 35 h. The mixture was fractionated in vacuo to give 1.63 g (81.3%) of Et_3GeBr (b.p. 64-66°/10 mm Hg, identified by GLC) and 4.46 g (65.6%) of IVb, b.p. 164-166°/1 mm Hg.

Compound IVa was prepared analogously.

Bis[tris(pentafluorophenyl)germyl] sulphide (Va)

A mixture of 3.61 g (5.53 mmol) of tris(pentafluorophenyl)germanium bromide and 0.90 g (2.55 mmol) of bis(triethylgermyl) sulphide was heated at 150° for 32 h. The volatile products were removed in vacuo and the residue recrystallized triply from hexane. 2.32 g (76.8%) of compound Va was obtained. GLC analysis of the volatile products showed 0.80 g (65.2%) of Et_3GeBr.

Compound Vb was prepared analogously.

Reaction of sulphur with hexakis(pentafluorophenyl)digermane

A mixture of 1.15 g (1.00 mmol) of $(C_6F_5)_3GeGe(C_6F_5)_3$ [16], 0.04 g (1.25 mmol) of sulphur and 6 ml of THF was heated at 60° for 3 h. Solid digermane completely dissolved. THF was removed and the solid residue was recrystallized twice from hexane. 0.61 g (51.6%) of Va was obtained, m.p. 165-167°. Mixed melting with a sample of Va obtained by reaction 5 gave no depression of melting point.

Under the similar conditions (100°, 5 h) hexakis(pentafluorophenyl)digermane reacts with selenium. Yield of compound Vb was 41.0%.

Tris(pentafluorophenyl)germyl[tris(pentafluorophenyl)stannyl] selenide (VIb)

A solution of 2.14 g (2.63 mmol) of IVb and 1.96 g (2.80 mmol) of $(C_6F_5)_3SnBr$ in 4 ml of toluene was heated at 100° for 2 h. GLC analysis of the volatile products gave 0.45 g (71.3%) of triethylgermanium bromide. After removal of the volatile products and the solvent the solid residue was recrystallized triply from hexane. 2.02 g (60.3%) of VIb was obtained.

Compound VIa was prepared analogously.

Reaction of Ia with diethylmercury

3.06 g (5.04 mmol) of Ia, 1.29 g (4.99 mmol) of diethylmercury and 4 ml of toluene were placed in an ampoule connected with gas burette. The mixture was kept at room temperature for 30 min and at 50° for 30 min. 69 ml (61.8%) of ethane evolved. The solution was decanted from the trace of generated mercury sulphide, the toluene was removed by condensation in vacuo and the residue was recrystallized twice from hexane. 2.55 g (61.2%) of $(C_6F_5)_3$-GeSHgEt (VII) was obtained.

The reaction of bis[tris(pentafluorophenyl)germyl]mercury with sulphur

A mixture of $[(C_6F_5)_3Ge]_2Hg$ (2.70 g, 2.00 mmol), sulphur (0.06 g, 1.87 mmol) and 6 ml of THF was heated at 50° for 1 h. The THF was removed in vacuo and the solid was recrystallized twice from hexane. 1.64 g (63.5%) of VIII was obtained.

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