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Dichlorobis(pentachlorophenyl)germane and derivatives; synthesis of bis(pentachlorophenyl)germanediol and molecular structure of diiodobis(pentachlorophenyl)germane

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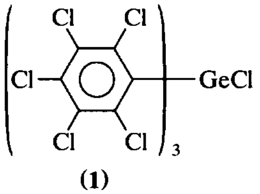
Abstract

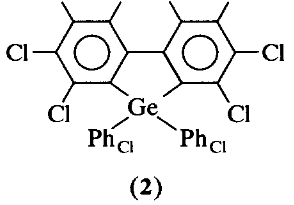
Dichlorobis(pentachlorophenyl)germane (**3**) has been prepared by reaction of $GeCl_4$ with either pentachlorophenyllithium or pentachlorophenylmagnesium chloride. After neutral hydrolysis of **3**, bis(pentachlorophenyl)germanediol (**8**) has been isolated and characterized as a stable solid. Thermal dehydration of **8** has been studied by thermogravimetry (TG) and differential scanning calorimetry (DSC), the product being $\{(C_6Cl_5)_2GeO\}_n$. Reaction of **3** with methanol leads to dimethoxybis(pentachlorophenyl)germane (**4**). Reduction of **3** with $LiAlH_4$ gives bis(pentachlorophenyl)germane (**5**) which, on treatment with Br_2 and I_2, gives dibromo- (**6**) and diiodobis(pentachlorophenyl)germane (**7**), respectively. The molecular structure of the diiodogermane 7 has been fully established by X-ray crystallography.

Key words: Germanium; Chlorine; pentachlorophenyl; X-ray diffraction

1. Introduction

Although much is known about organogermanium compounds bearing pentafluorophenyl groups [1–3], there were no reports of pentachlorophenyl organogermanium derivatives until our recent publications [4,5] describing chlorotris(pentachlorophenyl)germane (**1**) [4], obtained by reaction of germane tetrachloride and pentachlorophenyllithium, and perchloro (2,2′-biphenylene)diphenylgermane (**2**) [5], synthesized by treating **1** with pentachlorophenylmagnesium chloride. The molecular structures of both compounds were ascertained by X-ray analysis.


(**1**)


$Ph_{Cl}: C_6Cl_5$

(**2**)

In the course of our studies on these compounds and their derivatives, we observed the ease of cleavage of the carbon (aromatic)–germaniem bond due to pentachlorophenyl being such a good leaving group [4,5].

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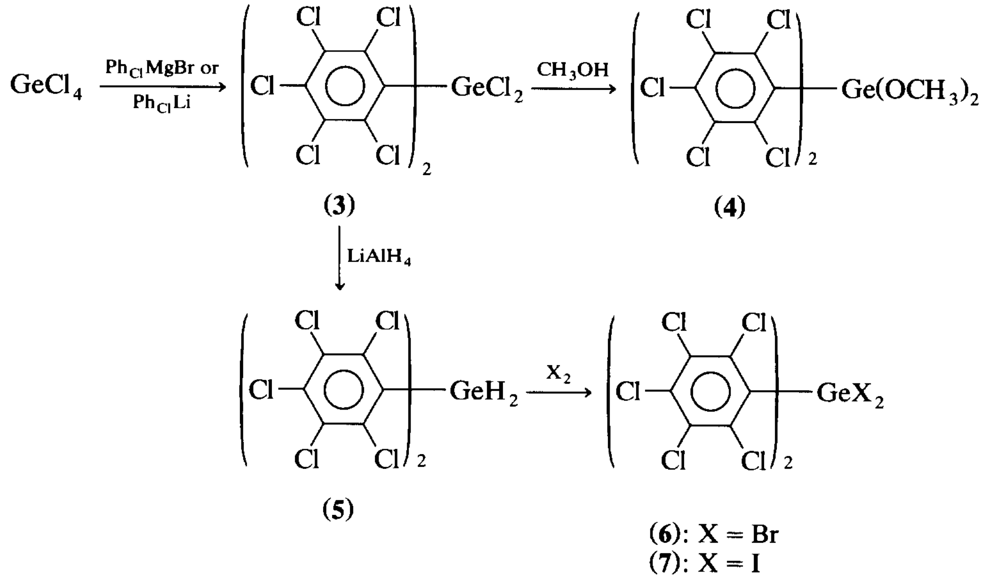
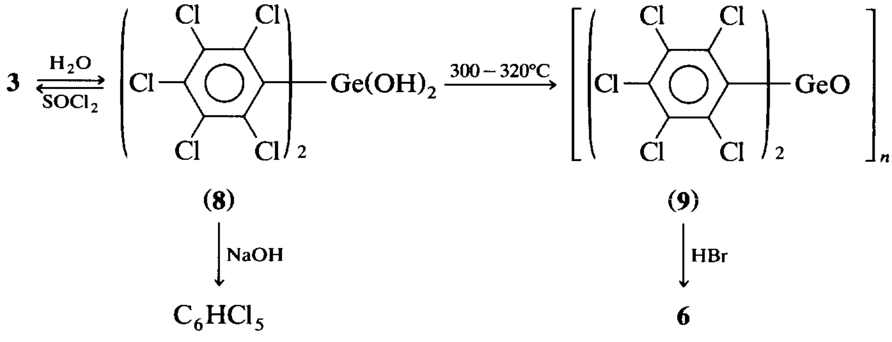


We now describe the synthesis of some bis(pentachlorophenyl)germanes and the remarkable preparation of bis(pentachlorophenyl)germanediol (**8**) the first diol of germanium isolated in solid state. The thermal behaviour of this germanediol **8** has been investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses. We also report the molecular structure of diiodobis(pentachlorophenyl)germane (**7**).

2. Results and discussion

Dichlorobis(pentachlorophenyl)germane (**3**) is readily prepared by treatment of tetrachlorogermane with either pentachlorophenyllithium or pentachlorophenylmagnesium chloride in a molar ratio 1:2. Germane **3** is reduced to bis(pentachlorophenyl)germane (**5**) by $LiAlH_4$ in THF at ambient temperature, and is converted into dimethoxygermane **4** by prolonged boiling of a solution in methanol. A tetrachloroethylene solution of **5** with bromine and iodine afforded the dibromo- and diiodogermanes **6** and **7**, respectively. All these new organogermanium compounds have been characterized by spectroscopic and elemental analyses, and the molecular structure of **7** has been elucidated by X-ray analysis.

As a general rule, the hydrolysis of dihalodiorganogermanes produces the oxides of the general formula $(R_2GeO)_n$ through the very ease dehydration of the corresponding dihydroxides which have only been detected in solution; evaporation of such solutions yields the oxides directly, as trimeric, tetrameric, and polymeric cyclic forms [6]. Even careful hydrolysis of dibromobis(pentafluorophenyl)germane with water gives bis(pentafluorophenyl)germanium oxide as a cyclic trimer [2]. In our case, and due to the influence of the steric and/or electron-withdrawing effects of the pentachlorophenyl group, a smooth and neutral hydrolysis of dichlorobis(pentachlorophenyl)germane (**3**) yielded a residue of bis(pentachlorophenyl)germanediol (**8**) from evaporation of a chloroform solution. This diol, characterized by IR, ^{1}H NMR, and mass spectra, and elemental analysis, was regenerated as **3** upon treatment with thionyl chloride. Treatment of germanediol **8** in THF with an aqueous NaOH solution yields pentachlorobenzene in a nearly quantitative yield, and



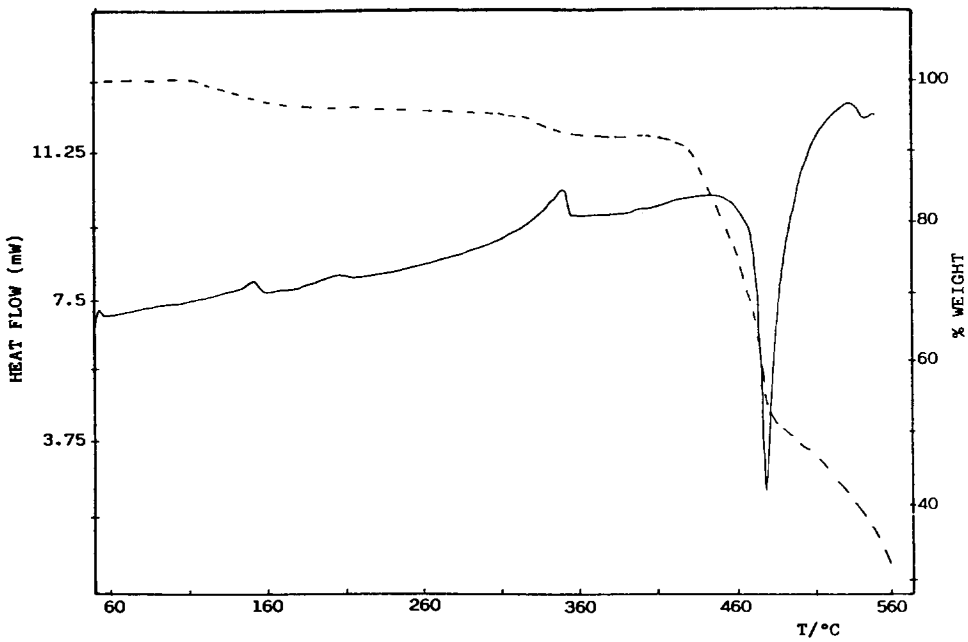


Fig. 1. TG (broken line) and DSC (full line) curves for bis(pentachlorophenyl)germanediol (**8**) recorded under N_2 at heating rates of 10.0°C/min and 20.0°C/min.

dehydration of **8** on heating gives the oxide **9**. An aqueous HBr solution converts the oxide **9** to the dibromogermane **6**. In contrast to **8**, the oxide **9** does not react with thionyl chloride under similar reaction conditions.

The EI mass spectrum of diol **8** shows the molecular ion peak (M^+, $C_{12}H_2{}^{35}Cl_{10}{}^{74}GeO_2$, 602) and two characteristic peaks ($M^+ - OH$, 585; $M^+ - Cl$, 567), all with the isotopic distributions in accordance with the theoretical calculations.

Figure 1 shows the TG and DSC curves for a sample of bis(pentachlorophenyl)germanediol. The first weight-loss observed in the TG curve at about 120°C corresponds to a small endothermic peak in the DSC curve and represents the loss of residual organic solvent (IR evidence). After this first process, the weight remains constant until 300°C, although the DSC curve shows a very smooth endothermic peak at about 200°C which may correspond to a rearrangement of the crystal structure of **8** since a sample of this diol did not melt at temperatures as high as 340°C (Köfler microscope). Dehydration to oxide **9** (IR evidence) occurs at about 310°C with a weight loss of approximately 3.5% which corresponds to an endothermic peak in the DSC curve; in the IR spectrum, the oxide exhibits a characteristic strong germanium–oxygen absorption band at 820 cm^{-1} which is not observed in the spectrum of diol **8**. The chemical decomposition of oxide **9** occurs at *ca.* 430°C and corresponds to a large exothermic peak in the DSC curve. At 590°C, the weight of the residue left in the TG experiment corresponded to complete degradation to GeO_2. An isothermal experiment on the bench with the oxide at 430°C gave a sublimate identified by HPLC as hexachlorobenzene, along with minor proportions of pentachlorobenzene and perchlorobiphenyl.

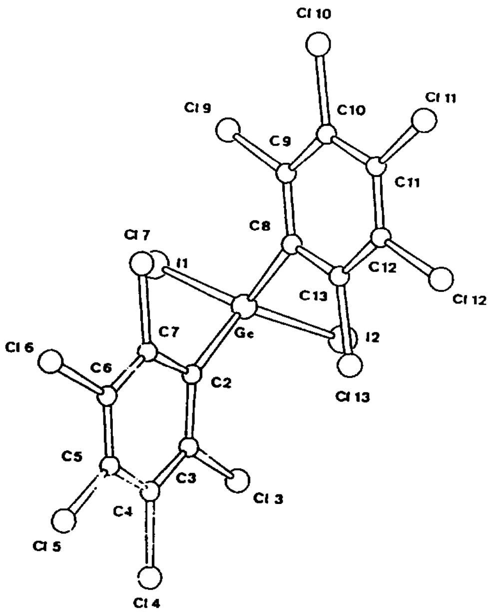


Fig. 2. The molecular structure of diiodobis(pentachlorophenyl)germane (7) with the atom numbering scheme.

TABLE 1. Bond distances (Å) and angles (°) with standard deviations in parentheses for 7

Bond distances (Å)			
Ge–C(2)	1.954(12)	Ge–C(8)	1.954(11)
C(2)–(C3)	1.420(16)	C(8)–C(9)	1.415(15)
C(3)–Cl(3)	1.714(4)	C(9)–Cl(9)	1.742(11)
C(3)–C(4)	1.399(18)	C(9)–C(10)	1.353(18)
C(4)–Cl(4)	1.716(12)	C(10)–Cl(10)	1.716(12)
C(4)–C(5)	1.351(19)	C(10)–C(11)	1.433(15)
C(5)–Cl(5)	1.718(13)	C(11)–Cl(11)	1.737(12)
C(5)–C(6)	1.424(17)	C(11)–C(12)	1.336(16)
C(6)–Cl(6)	1.733(14)	C(12)–Cl(12)	1.733(10)
C(6)–C(7)	1.333(18)	C(12)–C(13)	1.410(16)
C(7)–Cl(7)	1.706(12)	C(13)–Cl(13)	1.727(11)
C(7)–C(2)	1.441(19)	C(13)–C(8)	1.369(14)
Ge–I(1)	2.518(1)	Ge–I(2)	2.502(2)
Bond angles (°)			
I(1)–Ge–C(2)	101.3(0.3)	I(2)–Ge–C(8)	100.0(0.4)
Ge–C(2)–C(3)	127.3(1.0)	Ge–C(8)–C(9)	127.3(0.8)
C(2)–C(3)–C(4)	121.7(1.2)	C(8)–C(9)–C(10)	124.6(1.1)
C(3)–C(4)–C(5)	120.6(1.1)	C(8)–C(10)–C(11)	118.9(1.6)
C(4)–C(5)–C(6)	119.0(1.2)	C(10)–C(11)–C(12)	118.3(1.0)
C(5)–C(6)–C(7)	121.5(1.3)	C(11)–C(12)–C(13)	121.5(1.0)
C(6)–C(7)–C(2)	121.7(1.1)	C(12)–C(13)–C(8)	122.1(1.0)
C(7)–C(2)–C(3)	115.3(1.1)	C(13)–C(8)–C(9)	115.0(1.0)
C(7)–C(2)–Ge	117.4(0.9)	C(13)–C(8)–Ge	117.6(0.8)
C(2)–C(3)–Cl(3)	119.6(1.0)	C(8)–C(9)–Cl(9)	117.3(0.9)
Cl(3)–C(3)–C(4)	118.7(0.9)	Cl(9)–C(9)–C(10)	118.6(0.9)
C(3)–C(4)–Cl(4)	118.8(1.0)	C(9)–C(10)–Cl(10)	121.0(0.9)
Cl(4)–C(4)–C(5)	120.5(1.0)	Cl(10)–C(10)–C(11)	120.0(1.0)
C(4)–C(5)–Cl(5)	121.3(1.0)	C(10)–C(11)–Cl(11)	118.2(0.9)
Cl(5)–C(5)–C(6)	119.6(1.1)	Cl(11)–C(11)–C(12)	123.5(0.9)
C(5)–C(6)–Cl(6)	117.9(1.0)	C(11)–C(12)–Cl(12)	118.7(0.9)
Cl(6)–C(6)–C(7)	120.5(1.0)	Cl(12)–C(12)–C(13)	119.7(0.9)
C(6)–C(7)–Cl(7)	120.6(1.1)	C(12)–C(13)–Cl(13)	117.2(0.8)
Cl(7)–C(7)–C(2)	117.6(1.0)	Cl(13)–C(13)–C(8)	120.4(0.9)
C(2)–Ge–I(2)	122.8(0.4)	C(8)–Ge–I(1)	123.4(0.3)
C(2)–Ge–C(8)	109.0(0.5)	I(1)–Ge–I(2)	102.0(0.1)

The structure of the molecule of diiodobis(pentachlorophenyl)germane (**7**) is shown in Fig. 2, and the bond distances and angles are listed in Table 1. There is considerable distortion of the tetrahedral environment around the Ge atom. Whereas bond angles I(1)GeI(2) (102.02°), I(1)GeC(2) (102.2°), and I(2)GeC(8) (100.4°) are a little smaller than the ideal value and angle C(2)GeC(8) (109.0°) is ideal, angles I(1)GeC(8) (122.6°) and I(2)GeC(2) (122.5°) are much greater, which may be due to the steric repulsions between I(1)–Cl(9) and I(2)–Cl(3). Accordingly, the distances between the iodine and chlorine atoms in these pairs of atoms are shorter than the sums of van der Waals radii, as shown in Table 2.

TABLE 2. Some characteristic distances between atoms in the molecular structure of 7 (Å) [a]

I(1) ··· Cl(9)	3.557
I(1) ··· Cl(7)	3.731
I(2) ··· Cl(3)	3.551
I(2) ··· Cl(13)	3.879

[a] van der Waals radii [8], I: 2.15; Cl: 1.80 Å.

The Ge–I bond distances (2.52 and 2.50 Å) are similar to other reported values [7] and consistent with the sum of covalent radii (1.22 for Ge and 1.334 Å for I) [8]. The Cl–C and C–C bond distances are normal values for the pentachlorophenyl group.

3. Experimental details

Melting points were determined with a Köfler microscope and are uncorrected. IR spectra were recorded on Perkin Elmer 682 and 1330 spectrometers and UV spectra on a Beckmann Acta M-VI spectrometer. A Bruker WP 805Y was used for ^1H NMR spectroscopy. TG and DSC analyses were carried out with a Perkin Elmer TGS1 thermobalance under N_2 at a heating rate of 10°C/min, and with a Perkin Elmer DSC7 instrument at a heating rate of 20°C/min, respectively. Mass spectral data were obtained with a double focusing AEI M5-9025 spectrometer (70 eV, 100 μA emission). THF and benzene were freshly distilled from sodium, $SOCl_2$ was distilled before use, and the other solvents were used as received.

3.1. Dichlorobis(pentachlorophenyl)germane (3)

3.1.1. Synthesis from $GeCl_4$ and C_6Cl_5Li

Under argon, n-BuLi (32.5 ml of a 1.47 M solution in hexane, 47.8 mmol) was slowly added by syringe to a mixture of hexachlorobenzene (14 g, 49.2 mmol) and anhydrous diethyl ether (200 ml) at −20°C. The resulting solution was stirred (30 min) at −20°C and then transferred via cannula to a solution of $GeCl_4$ (5.08 g, 23.7 mmol) in ether (50 ml) at 0°C. The mixture was allowed to warm to room temperature and stirred for 18 h. The solvent was distilled off, benzene (150 ml) was added to the residue, the resulting mixture was heated under reflux for 2 h and the insoluble material was filtered off. The solution was evaporated to dryness and the residue, after vacuum sublimation of volatiles (hexachlorobenzene and pentachlorobenzene, 1.27 g), was recrystallized from benzene to give dichlorobis(pentachlorophenyl)germane (10.5 g, 69%), m.p. 251.5–252.5°C (sublimed at 230°C, 1 mmHg). IR (KBr): 1515m, 1340s, 1325s, 1300s, 1290s, 1260w, 1220w, 1200w, 1175m, 1157w, 1090m, 855s, 705w, 680s, 635w, 580w, 415s cm^{-1}. UV-Vis ($CHCl_3$) 287sh nm, 297, 307 (ϵ 1070, 2140, 2620). Mass spectrum: m/z 638 ($C_{12}{}^{35}Cl_{10}{}^{74}Ge$, M^+), 603 ($M^+ - Cl$), 568 ($M^+ - 2Cl$), 391 ($M^+ - C_6Cl_5$), 356 ($M^+ - Cl - C_6Cl_5$). Anal. Found: C, 22.5; Cl, 66.6. $C_{12}Cl_{12}Ge$ calcd.: C, 22.4; Cl, 66.3%.

3.1.2. Synthesis from $GeCl_4$ and C_6Cl_5MgCl

Under argon, a THF solution of pentachlorophenylmagnesium chloride [made from hexachlorobenzene (29 g, 0.1 mol), Mg (3.6 g, 0.15 mol) and THF (100 ml)] was added slowly to a stirred solution of $GeCl_4$ (12.2 g, 0.06 mol) in THF (40 ml). The mixture was stirred at ambient temperature for 16 h, and then the solvent was distilled off. Benzene (150 ml) was added to the residue, and the mixture was heated under reflux for 1 h. The insoluble material was filtered off, the solution was evaporated to dryness and the residue in hexane was filtered through silica gel. The resulting solution was evaporated to dryness, and the residue, after sublimation of volatiles (hexachlorobenzene and pentachlorobenzene, 5.69 g) was the required material (15.9 g, 44%).

3.2. Bis(pentachlorophenyl)germanediol (8)

3.2.1. Synthesis

A solution of dichlorobis(pentachlorophenyl)germane (0.92 g) in THF-H_2O (20 ml, 1:1) was stirred at reflux for 5 h, and then poured into an excess of H_2O and extracted with chloroform. The organic solution, dried over Na_2SO_4 and evaporated to dryness under vacuum, gave bis(pentachlorophenyl)germanediol (0.77 g, 89%). IR (KBr): 3640w, 1520m, 1340s, 1325s, 1300s, 1200w, 1175w, 1160w, 1090m, 915w, 870m, 855s, 710w, 700m, 695m, 680m, 625w, 608w, 585w cm^{-1}. UV-Vis ($CHCl_3$) 285sh nm, 295, 305 (ϵ 1250, 2030, 2330). ^1H NMR ($CDCl_3$): δ 3.39 (br.s). Mass spectrum: m/z 602 ($C_{12}H_2{}^{35}Cl_{10}{}^{74}GeO_2$, M^+), 585 ($M^+ - OH$), 567 ($M^+ - Cl$), 550 ($M^+ - Cl - OH$). Anal. Found: C, 24.0; H, 0.3; Cl, 58.5. $C_{12}H_2Cl_{10}GeO_2$ calcd.: C, 23.8; H, 0.3; Cl, 58.6%.

3.2.2. Hydrolysis

A mixture of bis(pentachlorophenyl)germanediol (0.11 g) and aqueous NaOH solution (10%) (2 ml) in THF (10 ml) was stirred at room temperature for 3 h, poured into an excess of H_2O, and the resulting mixture was extracted with chloroform. The organic solution, dried over Na_2SO_4 and evaporated under vacuum, gave pentachlorobenzene (0.08 g, 90%).

3.2.3. Reaction with $SOCl_2$

A solution of bis(pentachlorophenyl)germanediol (0.06 g) in distilled thionyl chloride (20 ml) was heated under reflux for 3 h under a dry atmosphere and then evaporated to dryness. The residue was treated with chloroform-H_2O, and the organic layer, dried over Na_2SO_4 and evaporated under vacuum, gave dichlorobis(pentachlorophenyl)germane (0.06 g, 99%).

3.3. Bis(pentachlorophenyl)germane (5)

3.3.1. Synthesis

Powdered $LiAlH_4$ (0.085 g, 2.23 mmol) was poured into a solution of dichlorobis(pentachlorophenyl)germane (1.50 g, 2.34 mmol) in THF (60 ml) and then stirred at room temperature for 3 h. The mixture was poured into dilute aqueous HCl and then extracted with chloroform. The organic layer, washed with H_2O, dried over Na_2SO_4 and evaporated under vacuum, gave bis(pentachlorophenyl)germane (1.30 g, 97%), m.p. 214–215°C (sublimed at 220°C, 0.3 mmHg). IR (KBr) 2160w, 2140w, 1515m, 1390w, 1365w, 1332s, 1320s, 1300s, 1200w, 1170w, 1162w, 1155w, 1090m, 855s, 760s, 730w, 702w, 675s, 665w, 615w, 475w cm^{-1} UV-Vis ($CHCl_3$) 282sh nm, 292, 302 (ϵ 740, 1350, 1570). ^1H NMR ($CDCl_3$): δ 6.08 (s). Mass spectrum: m/z 570 ($C_{12}H_2{}^{35}Cl_{10}{}^{74}Ge$, M^+) 323 ($M^+ - C_6Cl_5$). Anal. Found: C, 25.1; H, 0.4; Cl, 61.5. $C_{12}H_2Cl_{10}Ge$ calcd.: C, 25.1; H, 0.4; Cl, 61.8%.

3.3.2. Reaction with Br_2

A solution of bromine (0.13 g, 0.81 mmol) and bis(pentachlorophenyl)germane (0.361 g, 0.63 mmol) in tetrachloroethylene (25 ml) was heated under reflux under a dry atmosphere for 3 h and then evaporated to dryness under vacuum to give dibromobis(pentachlorophenyl)germane (0.457 g, 99%), m.p. 230–233°C (sublimed at 220–230°C, 0.3 mmHg). IR (KBr) 1512m, 1335s, 1322s, 1315s, 1295s, 1285s, 1255w, 1215w, 1200w, 1170w, 1155w, 1088m, 852s, 708w, 680s, 630w, 590w, 580w, 415w cm^{-1}. IR (polyethylene-Nujol) 350w, 305m, 265m cm^{-1}. UV-Vis ($CHCl_3$) 287sh nm, 298, 307 (ϵ 1020, 1970, 2400). Mass spectrum: m/z 726 ($C_{12}{}^{79}Br_2{}^{35}Cl_{10}{}^{74}Ge$, M^+), 647 ($M^+ - Br$), 479 ($M^+ - C_6Cl_5$). Anal. Found: C, 20.1; Br, 21.7; Cl, 48.6. $C_{12}Br_2Cl_{10}Ge$ calcd.: C, 19.7; Br, 21.9; Cl, 48.5%.

3.3.3. Reaction with I_2

A solution of iodine (0.278 g, 1.10 mmol) and bis(pentachlorophenyl)germane (0.282 g, 0.49 mmol) in tetrachloroethylene (20 ml) was heated under reflux under a dry atmosphere for 3 days and then evaporated to dryness under vacuum to give diiodobis(pentachlorophenyl)germane (0.427 g, 100%), m.p. 228–231°C (sublimed at 220°C; 0.1–0.2 mmHg). IR (KBr): 1510m, 1335s, 1320s, 1315s, 1295s, 1285s, 1255w, 1198w, 1170w, 1155w, 1082m, 848s, 705w, 675s, 625w, 582w cm^{-1}. IR (polyethylene-Nujol) 350m, 270s, 240m cm^{-1}. UV-Vis ($CHCl_3$) 289sh nm, 298, 307 (ϵ 4440, 4990, 4620). Mass spectrum: m/z 822 ($C_{12}{}^{35}Cl_{10}I_2{}^{74}Ge$, M^+), 695 ($M^+ - I$), 568 ($M^+ - 2I$), 321 ($M^+ - 2I - C_6Cl_5$). Anal. Found: C, 17.4; Cl 43.5; I, 30.5. $C_{12}Cl_{10}GeI_2$ calcd.: C, 17.5; Cl, 43.0; I, 30.8%.

3.4. Bis(pentachlorophenyl)germanium oxide (9)

3.4.1. Synthesis

Bis(pentachlorophenyl)germanediol (0.093 g), heated at 300–320°C for 2 h, gave bis(pentachlorophenyl) germanium oxide (0.090 g, 100%), dec. *ca.* 460°C (DSC). IR (KBr): 1515m, 1395w, 1340s, 1328s, 1305s, 1220w, 1202w, 1175w, 1165w, 1090m, 870m, 858s, 820s, 710w, 680m, 630w, 608w, 585w, 560w cm^{-1}. UV-Vis ($CHCl_3$) 285sh nm, 295, 305 (ϵ 370, 700, 810). Anal. Found: C, 24.6; Cl, 60.1. $C_{12}Cl_{10}GeO$ calcd.: C, 24.5; Cl, 60.4%.

3.4.2. Reaction with HBr

A mixture of bis(pentachlorophenyl)germanium oxide (0.092 g) and aqueous HBr (48%) (20 ml) was stirred at reflux for 4 days, and then poured into H_2O. The resulting mixture was extracted with chloroform and the organic layer, washed with H_2O, dried over Na_2SO_4 and evaporated under vacuum, gave dibromobis(pentachlorophenyl)germane (0.044 g, 39%).

3.4.2. Treatment with $SOCl_2$

A mixture of bis(pentachlorophenyl)germanium oxide (0.162 g) and thionyl chloride (20 ml) was stirred at reflux for 3 h and then evaporated to dryness, giving **9** quantitatively.

3.5. X-ray crystallography of 7

3.5.1. Crystal data

$C_{12}C_{10}GeI_2$, $M_r = 825.08$, space group $P2_1/C$, $a = 8.71$, $b = 20.92$, $c = 11.84$ Å, $\alpha = \gamma = 90°$, $\beta = 98.25°$, $V = 2135.35$ Å^3, $Z = 4$, $D_c = 2.54$ g/cm^3. Well formed crystals, 1.0 × 0.25 × 0.25 mm. μ(Mo K_α) = 42.13 cm^{-1}.

3.5.2. Intensity data collection, structure solution and refinement

Space group and cell parameters were determined from 25 reflections ($5 < \theta < 15°$) measured on an Enraf-Nonius CAD-4 diffractometer installed on an Elliot G × 21 rotating anode generator running at 2.4 kW and using Cu K_α radiation ($\lambda = 1.5418$ Å) with a graphite monochromator. A first data set consisting of 8398 reflections was measured at room temperature from a crystal measuring 1.0 × 0.25 × 0.25 mm, in the ω-scan mode.

Three reflections measured every hour during the data collection showed no significant change in intensity. Lorentz, polarization, decay and empirical absorption corrections were applied in derivation of the structure factor amplitudes. After merging and averaging with the program SHELXS86 [9], 3950 reflections were considered independent being the R_{sym} value 8.21%.

The structure was solved by direct methods using SHELXS86. The first E-map clearly revealed the two iodine atoms and the germanium atom at the central part of the molecule. Tangent phase recycling using these three atoms led to the location of the rest of the molecule except for one carbon atom. This carbon atom (C5) was located in a difference Fourier map after least squares refinement. After several cycles of full matrix refinement with anisotropic temperature factors for all atoms the standard agreement factor was $R = 12.53\%$ for 2976 reflections with $I > 5\sigma(I)$. However most anisotropic temperature factors did not converge properly and large shifts were observed in each cycle.

A second data set was collected from a crystal measuring 0.5 × 0.2 × 0.2 mm on a CAD-4 diffractometer using Mo Kα radiation ($\lambda = 0.7093$ Å). 6660 reflections were measured up to a theta angle of 30°, at room temperature. Using the coordinates from the previously refined structure in the last isotropic refinement cycle, full matrix least squares refinement followed with the Mo radiation data set. After isotropic

TABLE 3. Fractional atomic coordinates with estimated standard deviations in parentheses and equivalent isotropic thermal parameters for 7

ATOM	x	y	z	B_{eq}
Ge	0.3452(1)	0.8109(1)	0.1820(1)	2.57
C(2)	0.2086(14)	0.8553(6)	0.0619(9)	2.67
C(3)	0.0747(13)	0.8304(7)	−0.0065(10)	2.73
C(4)	−0.0066(13)	0.8656(7)	−0.0961(10)	2.95
C(5)	0.0357(13)	0.9262(7)	−0.1168(10)	2.85
C(6)	0.1640(12)	0.9538(7)	−0.0453(11)	3.05
C(7)	0.2446(13)	0.9210(7)	0.0396(11)	3.12
Cl(3)	0.0141(4)	0.7542(2)	0.0172(3)	4.29
Cl(4)	−0.1663(5)	0.8318(2)	−0.1756(4)	5.06
Cl(5)	−0.0683(4)	0.9715(2)	−0.2222(3)	4.25
Cl(6)	0.2172(4)	1.0312(2)	−0.0751(3)	3.83
Cl(7)	0.4011(3)	0.9543(2)	0.1216(3)	3.79
I(1)	0.5845(1)	0.7956(1)	0.0886(1)	4.54
C(8)	0.3449(13)	0.8567(6)	0.3258(9)	2.63
C(9)	0.4752(12)	0.8752(6)	0.4044(10)	2.44
C(10)	0.4661(13)	0.9073(6)	0.5023(11)	2.96
C(11)	0.3161(13)	0.9230(6)	0.5307(10)	2.83
C(12)	0.1910(12)	0.9038(6)	0.4602(10)	2.56
C(13)	0.2041(11)	0.8723(6)	0.3568(10)	2.43
Cl(9)	0.6576(3)	0.8534(2)	0.3732(3)	4.45
Cl(10)	0.6300(4)	0.9260(2)	0.5951(3)	4.21
Cl(11)	0.3070(4)	0.9669(2)	0.6507(3)	3.88
Cl(12)	0.0095(4)	0.9158(2)	0.5002(3)	3.77
Cl(13)	0.0343(3)	0.8474(2)	0.2752(3)	3.29
I(2)	0.2934(1)	0.6997(0)	0.2448(1)	4.29

refinement, the data were corrected for absorption with the computer program DIFABS [10]. Anisotropic refinement converged to a final R factor of 3.58% ($R_w = 4.83\%$) for 4573 reflections with $I > 4\sigma(I)$. The weighting scheme used in the last cycle was $(\sigma^2(F) + 0.017564\ |F|^2)^{-1}$ and the maximum shift/e.s.d. was 0.006. All cycles of least squares refinement and difference Fourier syntheses were carried out with the SHELXS76 computer program [11]. A Microvax 3100 was used for all calculations. The atomic parameters are given in Table 3. Structure factors are available from the authors, and the crystallographic data have also been deposited at the Cambridge Crystallographic Data Centre.

3.6. Dimethoxybis(pentachlorophenyl)germane (4)

A mixture of dichlorobis(pentachlorophenyl)germane (0.418 g, 0.65 mmol) and methanol (80 ml) was stirred at reflux for 7 d, and then evaporated under vacuum to give dimethoxybis(pentachlorophenyl)germane (0.40 g, 97%), m.p. 201–204°C (from methanol). IR (KBr) 2960w, 2935w, 2925w, 2895w, 2830w, 2820w, 1515m, 1450w, 1440w, 1395w, 1340s, 1325s, 1300s, 1255w, 1220w, 1200w, 1170w, 1158w, 1090m, 1058m, 1035s, 868w, 855s, 708w, 680s, 632w, 622w, 605m, 582w cm^{-1}. UV-Vis ($CHCl_3$): 284sh nm, 294, 304 (ϵ 990, 1890, 2270). ^1H NMR ($CDCl_3$): δ 3.68 (s). Anal. Found: C, 26.6; H, 0.8; Cl, 56.4. $C_{14}H_6Cl_{10}GeO_2$ calcd.: C, 26.6; H, 1.0; Cl 56.0%.

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