

Alkyl- and aryl-sulphinylmethylgermanium compounds $\text{Ph}_3\text{GeCH}_2\text{S}(\text{O})\text{R}$: structure of $\text{Ph}_3\text{GeCH}_2\text{S}(\text{O})\text{C}_6\text{H}_4^t\text{Bu-}p$

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Received 23 November 1995

Abstract

Triphenyl[(organosulphinyl)methyl]germanium compounds [$\text{Ph}_3\text{GeCH}_2\text{S}(\text{O})\text{R}$: 1 R = Me, $\text{C}_6\text{H}_4\text{X-}p$, X = H, Me or ^tBu] have been prepared by oxidation of the corresponding sulphido compounds, $\text{Ph}_3\text{GeCH}_2\text{SR}$, with *m*-chloroperbenzoic acid. Further oxidation of 1 by *m*- $\text{ClC}_6\text{H}_4\text{CO}_3\text{H}$ produces the corresponding sulphones, $\text{Ph}_3\text{GeCH}_2\text{S}(\text{O})_2\text{R}$. Compounds (1 R = Me or $\text{C}_6\text{H}_4^t\text{Bu-}p$) are extensively decomposed on heating to 170°C. A crystal structure determination of (1 R = $\text{C}_6\text{H}_4^t\text{Bu}$) indicated it to be a molecular species with a tetrahedral geometry at germanium. The S–O bond is twisted out of the plane of the attached aryl ring by 7.0(3)°.

Keywords: Germanium; Sulfoxide; Sulphinylmethyl derivatives; Crystal structure

1. Introduction

There have been few studies of (organosulphinylmethyl)germanium compounds $\text{R}'_3\text{GeCH}_2\text{S}(\text{O})\text{R}$. These reports have been limited to trimethyl[(phenylsulphinyl)methyl]germanium [$\text{Me}_3\text{GeCH}_2\text{S}(\text{O})\text{Ph}$], obtained from $\text{Me}_3\text{GeCH}_2\text{Cl}$ on successive reactions with Mg and $\text{PhS}(\text{O})\text{OMe}$ [1], and to [$\text{Ph}_3\text{GeCH}_2\text{S}(\text{O})\text{C}_6\text{H}_4\text{Me-}p$: 1 R = $\text{C}_6\text{H}_4\text{Me-}p$], produced on oxidation of $\text{Ph}_3\text{GeCH}_2\text{SC}_6\text{H}_4\text{Me-}p$ by Br_2 in aqueous MeOH [2]. Compounds $\text{R}'_3\text{GeCH}_2\text{S}(\text{O})\text{R}$ are reported to be considerably more resistant to hydrolysis than the silicon analogues $\text{R}'_3\text{SiCH}_2\text{S}(\text{O})\text{R}$ [1,3,4], e.g. $\text{Me}_3\text{GeCH}_2\text{S}(\text{O})\text{Ph}$ was only hydrolysed at 60°C over a prolonged period (50 days) [1], in contrast to the ready hydrolysis of $\text{R}'_3\text{SiCH}_2\text{S}(\text{O})\text{R}$ to $\text{MeS}(\text{O})\text{R}$ at ambient temperature. Thermolysis of $\text{R}'_3\text{SiCH}_2\text{S}(\text{O})\text{R}$ also occurs under particularly mild conditions, e.g. $\text{Me}_3\text{SiCH}_2\text{S}(\text{O})\text{Ph}$ rearranges completely within 1 h at 60°C to $\text{Me}_3\text{SiOCH}_2\text{SPh}$ [3]. The greater thermal stability of $\text{Me}_3\text{GeCH}_2\text{S}(\text{O})\text{Ph}$ is shown by its recovery on being heated at 60°C for 6 days [3].

Silylated derivatives $\text{R}'_3\text{SiCR}^3\text{R}^2\text{S}(\text{O})\text{R}$ ($\text{R}^3, \text{R}^2 = \text{H}$, alkyl or aryl) have attracted considerably more attention

than their germanium counterparts and more routes to their formation have been published: these synthetic methods include (i) reactions of $\text{R}_3\text{SiCH}_2\text{MgX}$ with $\text{ArS}(\text{O})\text{OMe}$ [1], (ii) reactions of Me_3SiCl with $\text{PhS}(\text{O})\text{CHR}^2\text{Li}$ [3], (iii) oxidation of $\text{Me}_3\text{SiCH}_2\text{SPh}$ by *m*-chloroperbenzoic acid, *m*- $\text{ClC}_6\text{H}_4\text{CO}_3\text{H}$ [4], and (iv) successive reactions of $\text{Me}_3\text{SiCHR}^2\text{S}(\text{O})\text{Ph}$ with BuLi and RI [5].

m-Chloroperbenzoic acid has found wide use as an oxidant of organic sulphides and it has been used in this study to produce both alkyl- and aryl-sulphinylmethylgermanium derivatives [$\text{Ph}_3\text{GeCH}_2\text{S}(\text{O})\text{R}$] from $\text{Ph}_3\text{GeCH}_2\text{SR}$. In addition to reporting some oxidation, spectral and stability results for (1 R = Me or $\text{C}_6\text{H}_4\text{X-}p$, X = H, Me or ^tBu), we also wish to report the crystal structure of (1 R = $\text{C}_6\text{H}_4^t\text{Bu-}p$).

2. Experimental

IR spectra were recorded on a Philips Analytical PU9800 Fourier-transform spectrometer. Solution NMR spectra were obtained on a Bruker 250 MHz instrument. A Polymer Laboratory DSC instrument was used. The compounds, $\text{Ph}_3\text{GeCH}_2\text{Cl}$ [6] and $\text{Ph}_3\text{GeCH}_2\text{SC}_6\text{H}_4\text{-Me-}p$ [7], were obtained by published procedures.

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2.1. Preparation of $\text{Ph}_3\text{GeCH}_2\text{SMe}$

A solution of Ph_3GeBr (12.9 g, 0.500 mol) in THF (75 ml) was slowly added, with stirring, to the Grignard reagent, prepared from MeSCH_2Cl (5.10 g, 0.0530 mol), Mg (2.75 g, 0.110 mol) in THF (50 ml). After complete addition, the reaction mixture was left overnight and hydrolysed with aqueous NH_4OH solution. The organic layer was collected, dried over MgSO_4 and rotary evaporated. The residue was crystallised from EtOH to give the title compound: yield, 10.1 g (55%); m.p. 85–87°C.

Anal. Found: C, 66.0; H, 5.7; S, 8.9%. $\text{C}_{20}\text{H}_{20}\text{GeS}$
Calc.: C, 65.8; H, 5.5; S, 8.8%.

^1H NMR (250 MHz, CDCl_3): δ 2.16 [s, 3H, Me], 2.69 [s, 2H, CH_2], 7.27–7.40 [m, 9H, *m*- + *p*-phenyl-H], 7.45 [m, 6H, *o*-phenyl-H].

2.2. Preparation of (1 R = Me)

Solutions of $\text{Ph}_3\text{GeCH}_2\text{SMe}$ (10.0 g, 0.0274 mol), in CHCl_3 (40 ml) and *m*-chloroperbenzoic acid (0.0274 mol) in CHCl_3 (40 ml) were mixed. After leaving at room temperature for 3 h, the reaction mixture was washed (three times) with aqueous NaHCO_3 , dried over MgSO_4 and rotary evaporated. The residue was crystallised from EtOH: yield, 7.83 g (75%); m.p. 114–116°C.

Anal. Found: C, 63.3; H, 5.3; S, 8.5%. $\text{C}_{20}\text{H}_{20}\text{GeOS}$
Calc.: C, 63.0; H, 5.3; S, 8.4%.

^1H NMR (250 MHz, CDCl_3): δ 2.39 [br.d, 3H, $J_{(\text{H}-\text{H})} = 0.6$ Hz, Me], 3.09 [d, 1H, $J_{(\text{H}-\text{H})} = 12.8$ Hz] and 3.27 [d, d, 1H, $J_{(\text{H}-\text{H})} = 12.8$ Hz, $J_{(\text{H}-\text{H})} = 0.6$ Hz] (CH_2), 7.36–7.45 [m, 9H, *m*- + *p*-phenyl-H], 7.49–7.62 [m, 6H, *o*-phenyl-H].

^{13}C NMR (62.9 MHz, CDCl_3): δ 41.9, 42.8, 128.5 [C_m], 129.3 [C_p], 134.0 [C_i], 134.7 [C_o].

2.3. Preparation of $\text{Ph}_3\text{GeCH}_2\text{S(O)}_2\text{Me}$

Solutions of (1 R = Me) (5.36 g, 0.0147 mol) in CHCl_3 (20 ml) and *m*-chloroperbenzoic acid (0.0147 mol) in CHCl_3 (20 ml) were mixed. After leaving at room temperature for 3 h, the reaction mixture was washed (three times) with aqueous NaHCO_3 , dried over MgSO_4 and rotary evaporated. The residue was crystallised from EtOH: yield, 4.14 g (71%); m.p. 173–175°C.

Anal. Found: C, 60.7; H, 5.4; S, 8.2%. $\text{C}_{20}\text{H}_{20}\text{GeO}_2\text{S}$
Calc.: C, 60.5; H, 5.1; S, 8.1%.

IR (cm^{-1} , KBr): 1290, 1130.

^1H NMR (250 MHz, CDCl_3): δ 2.77 [s, 3H, Me], 3.51 [s, 2H, CH_2], 7.4–7.5 [m, 9H, *m*- + *p*-phenyl-H], 7.55–7.7 [m, 6H, *o*-phenyl-H].

2.4. Preparation of $\text{Ph}_3\text{GeCH}_2\text{SC}_6\text{H}_4^i\text{Bu-p}$

To a solution of sodium ethoxide, prepared from Na (0.33 g, 0.0144 mol) and EtOH (100 ml), was successively added *p*- $^i\text{BuC}_6\text{H}_4\text{SH}$ (2.40 g, 0.0144 mol) and $\text{Ph}_3\text{GeCH}_2\text{Br}$ (5.72 g, 0.0144 mol). The reaction mixture was heated under reflux overnight, hot filtered and rotary evaporated. The residue was recrystallised from EtOH: yield, 5.42 g (78%); m.p. 139–140.5°C.

Anal. Found: C, 71.8; H, 6.4; S, 6.7%. $\text{C}_{29}\text{H}_{30}\text{GeS}$
Calc.: C, 72.1; H, 6.3; S, 6.6%.

^1H NMR (250 MHz, CDCl_3): δ 1.43 [s, 9H, Me], 3.21 [s, 2H, CH_2], 7.27–7.56 [m, aryl] and 7.67–7.74 [m, aryl].

^{13}C NMR (62.9 MHz, CDCl_3): δ 16.3 [CH_2], 31.3 [Me], 34.3 [Me_3C], 125.7, 126.4, 128.3 [C_m], 129.4 [C_p], 134.9 [C_o], 135.4 [C_i], 136.7, 148.1.

2.5. Preparation of (1 R = $\text{C}_6\text{H}_4^i\text{Bu-p}$)

The title compound was obtained from $\text{Ph}_3\text{GeCH}_2\text{-SC}_6\text{H}_4^i\text{Bu-p}$ (4.83 g, 0.0100 mol) and *m*- $\text{ClC}_6\text{H}_4\text{CO}_3\text{H}$ (0.0100 mol) in CH_2Cl_2 (40 ml) and recrystallised from MeOH: yield, 4.14 g (83%); m.p. 152–155°C.

^1H NMR (250 MHz, CDCl_3): δ 1.32 [s, 9H, Me], 3.26 [d, 1H, $J_{(\text{H}-\text{H})} = 12.9$ Hz] and 3.53 [d, 1H, $J_{(\text{H}-\text{H})} = 12.9$ Hz] (CH_2), 7.27–7.48 [m, aryl].

^{13}C NMR (62.9 MHz, CDCl_3): δ 31.1 [Me], 34.8 [Me_3C], 45.7 [CH_2], 123.8, 127.9, 128.3 [C_m], 129.3 [C_p], 134.3, 134.5 [C_i], 134.9 [C_o], 143.3.

2.6. Preparation of (1 R = $\text{C}_6\text{H}_4\text{Me-p}$)

The title compound was obtained from $\text{Ph}_3\text{GeCH}_2\text{-SC}_6\text{H}_4\text{Me-p}$ (1.76 g, 0.0040 mol) and *m*- $\text{ClC}_6\text{H}_4\text{CO}_3\text{H}$ (0.0040 mol) in CHCl_3 (40 ml): yield, 1.24 g (68%); m.p. 145–146°C. Lit. [2] m.p. 145–147°C.

Anal. Found: C, 68.6; H, 5.2; S, 7.5%. $\text{C}_{26}\text{H}_{24}\text{GeOS}$
Calc.: C, 68.4; H, 5.3; S, 7.4%.

IR (cm^{-1} , KBr): 1030. Lit. [2] value 1030.

^1H NMR (250 MHz, CDCl_3): δ 2.39 [s, 3H, Me], 3.20 [d, 1H, $J_{(\text{H}-\text{H})} = 12.9$ Hz], 3.36 [d, 1H, $J_{(\text{H}-\text{H})} = 12.9$ Hz] (CH_2), 7.10–7.60 [m, 19H, aryl].

^{13}C NMR (62.9 MHz, CDCl_3): δ 21.2 [Me], 46.0 [CH_2], 124.0, 128.3 [C_m], 129.3 [C_p], 129.6, 134.5 [C_i], 134.9 [C_m], 141.2, 143.5.

2.7. Preparation of $\text{Ph}_3\text{GeCH}_2\text{SPh}$

To a solution of Ph_3GeLi in THF, obtained from Ph_3GeBr (3.83 g, 0.0100 mol) and Li (0.70 g, 0.10 mol), was added, with stirring, a solution of PhSCH_2Cl (1.59 g, 0.0100 mol) in THF (100 ml). The resulting solution was left for 20 min, hydrolysed with aqueous NH_4Cl solution and the organic layer collected, dried over Na_2SO_4 and rotary evaporated. The residue was

recrystallised successively from EtOH and CHCl₃/pet. ether (60–80°C): yield, 2.01 g (47%); m.p. 127–128°C.

Anal. Found: C, 70.2; H, 5.0; S, 7.5%. C₂₅H₂₂GeS
Calc.: C, 70.3; H, 5.1; S, 7.5%.

¹H NMR (250 MHz, CDCl₃): δ 3.06 [s, 2H, CH₂], 7.1–7.8 [m, 20H, aryl].

¹³C NMR (62.9 MHz, CDCl₃): δ 15.7 [CH₂], 124.8, 126.1, 128.3 [C_m], 128.6, 129.4 [C_p], 134.9 [C_o], 135.2 [C_i], 140.1.

2.8. Preparation of (1 R = Ph)

A solution of Br₂ (0.384 g, 0.00240 mol) in MeOH:H₂O (25 ml, 1:1 v:v) was added dropwise to a stirred solution of Ph₃GeCH₂SPh (1.03 g, 0.00240 mol) in Et₂O (20 ml). After addition was complete, the ether layer was collected, dried over Na₂SO₄ and rotary evaporated. The residue was chromatographed (TLC: CHCl₃ as eluant). The title compound was obtained as a colourless solid: yield, 0.77 g (73%); m.p. 140–142°C.

Anal. Found: C, 67.1; H, 5.4; S, 7.2%. C₂₅H₂₂GeOS
Calc.: C, 67.4; H, 5.3; S, 7.2%

IR (cm⁻¹, KBr) = 1030.

¹H NMR (250 MHz, CDCl₃): δ 3.23 [d, 1H, J_(H-H) = 12.9 Hz], 3.35 [d, 1H, J_(H-H) = 12.9 Hz] (CH₂), 7.10–7.60 [m, 20H, aryl].

2.9. Preparation of Ph₃GeCH₂S(O)₂Ph

The title compound was obtained from (1 R = Ph) (0.600 g, 1.35 mmol) and *m*-ClC₆H₄CO₃H (1.35 mmol) in CH₂Cl₂ (20 ml). After leaving at room temperature for 3 h, the reaction mixture was washed (three times) with aqueous NaHCO₃, dried over MgSO₄ and rotary evaporated. The residue was crystallised from EtOH: yield, 0.43 g (69%); m.p. 195–198°C.

Anal. Found: C, 65.3; H, 4.9; S, 6.8%. C₂₅H₂₂GeO₂S
Calc.: C, 65.1; H, 4.8; S, 7.0%.

IR (cm⁻¹, KBr): 1305, 1148.

¹H NMR (250 MHz, CDCl₃): δ 3.60 [s, 2H, CH₂], 7.3–7.45 [m, aryl], 7.5–7.6 [m, aryl], 7.8–7.85 [m, aryl].

¹³C NMR (62.9 MHz, CDCl₃): δ 46.9 [CH₂], 126.8, 128.3 [C_m], 129.0, 129.6 [C_p], 132.8, 134.0 [C_i], 135.0 [C_o], 142.8.

2.10. Crystal structure determination of (1 R = C₆H₄ⁱBu-*p*)

The unit cell and intensity data were collected on a Delft Instruments FAST diffractometer using the routines ENDEX, REFINE and MADONL in the MADNES [8] software and processed using ABSMAD [9]; detailed procedures have been described [10]. The structure was solved with SHELX-86 [11] and the non-H atoms were refined with anisotropic temperature factors using

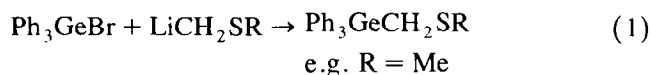
Table 1
Crystal data and structure refinement

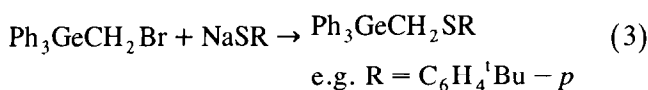
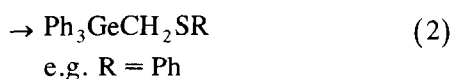
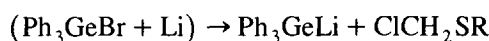
Empirical formula	C ₂₉ H ₃₀ GeOS
Formula weight	499.18
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	
<i>a</i> (Å)	15.169(8)
<i>b</i> (Å)	9.210(5)
<i>c</i> (Å)	18.952(5)
β (°)	102.20(3)
Volume (Å ³)	2588(2)
<i>Z</i>	4
Density (calculated) (Mg m ⁻³)	1.281
Absorption coefficient (mm ⁻¹)	1.282
<i>F</i> (000)	1040
Crystal size (mm ³)	0.43 × 0.14 × 0.11
θ range for data collection	2.20–25.00°
Index ranges	–15 ≤ <i>h</i> ≤ 16; –8 ≤ <i>k</i> ≤ 10; –21 ≤ <i>l</i> ≤ 20
Reflections collected	9786
Independent reflections	3948 [<i>R</i> _{int} = 0.0536]
Observed reflections (<i>I</i> > 2σ(<i>I</i>))	2277
Refinement method	Full-matrix least-squares on <i>F</i> ²
Number of parameters	300
Goodness-of-fit on <i>F</i> ² (S)	0.807
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0445, <i>wR</i> ₂ = 0.0906
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0772, <i>wR</i> ₂ = 0.0996
Final weighting scheme	Calc <i>w</i> = 1/ [σ ² (<i>F</i> _o ²) + (0.0370 <i>P</i>) ²] where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
Residual diffraction max. (e Å ⁻³)	0.692
Residual diffraction min. (e Å ⁻³)	–0.219

SHELXL-93 [12]. Disordered atoms were refined with population parameters of 0.333. Hydrogen atoms were allowed to ride on their attached carbon atoms with one of two common isotropic temperature factors. A molecular plot was obtained using the program ZORTEP [13]. Data collection and structure refinement parameters are given in Table 1. Tables of thermal parameters and hydrogen atom coordinates and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

Compounds Ph₃GeCH₂SR were obtained by the reactions shown in Eqs. (1)–(3).





An earlier report indicated that Ph₃GeCH₂SC₆H₄Me-p could be oxidised to (1 R = C₆H₄Me-p) using Br₂ in aqueous MeOH, but only in low yield [2]. Bromine in aqueous methanol, although a general and good oxidant for organic sulphides [14], was found in this study to be generally inefficient with Ph₃GeCH₂SR compounds. Even with excess Br₂, only poor yields of (1) were obtained. Sodium metaperiodate was, however, even less effective, with no (1) being isolated using this oxidant in mixed phase water/dichloromethane systems. In contrast, *m*-chloroperbenzoic acid (1 equivalent) was found to be a mild and effective reagent for the formation of both alkyl- and aryl-sulphinylmethyl-germanium compounds (1 R = Me, C₆H₄R¹-p, R¹ = H, Me or ¹Bu) from Ph₃GeCH₂SR. No cleavage of phenyl-germanium bonds occurred during these reactions. Further oxidation of the sulfoxides (1) to the sulphones Ph₃GeCH₂S(O)₂R also occurs smoothly using *m*-ClC₆H₄CO₃H. As reported in the Introduction, *m*-chloroperbenzoic acid has also been found to be a useful oxidant for R₃SiCH₂SR [4].

The $\nu(\text{SO})$ values for (1) are about 1030 cm⁻¹ and are within the region established for organic sulfoxides [15]. The CH₂ protons are diastereotopic, due to the adjacent sulfoxide group, with $J_{(\text{H}-\text{H})}$ values of ca. 13 Hz. Values of $J_{(\text{H}-\text{H})}$ for other XCH₂S(O)Ar species are 13.5 Hz [R₃SiCH₂S(O)R] [1], 12.5 Hz [Me₃GeCH₂S(O)Ph] [1] and 10.8 Hz [ICH₂S(O)Ar] [16].

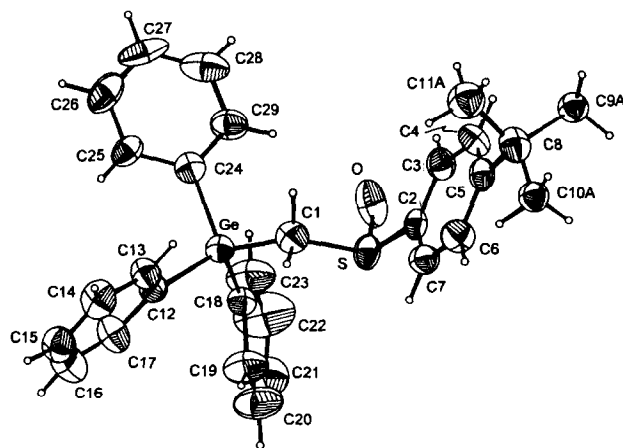


Fig. 1. Atom arrangement and numbering system for (1 R = C₆H₄¹Bu-p).

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	U_{eq}
Ge	3355.2(3)	1409.2(4)	1282.3(2)	47(1)
S	1499(1)	2538(1)	371(1)	60(1)
O	1392(2)	1061(4)	28(2)	92(1)
C(1)	2147(3)	2205(5)	1252(2)	61(1)
C(2)	449(3)	2960(5)	619(2)	48(1)
C(3)	-208(3)	1933(5)	549(2)	58(1)
C(4)	-994(3)	2217(5)	782(3)	62(1)
C(5)	-1147(3)	3531(5)	1094(2)	53(1)
C(6)	-472(4)	4584(5)	1129(3)	65(1)
C(7)	309(3)	4295(5)	898(3)	59(1)
C(8)	-1976(3)	3774(5)	1412(2)	68(1)
C(9A)	-2821(8)	3198(16)	906(7)	51(4)
C(10A)	-2122(11)	5410(9)	1534(9)	58(4)
C(11A)	-1816(12)	2979(18)	2136(6)	79(5)
C(9B)	-1649(10)	3874(18)	2244(5)	78(5)
C(10B)	-2701(11)	2653(15)	1225(10)	108(7)
C(11B)	-2354(14)	5312(12)	1178(10)	137(10)
C(9C)	-2800(10)	3748(19)	778(7)	97(8)
C(10C)	-2066(13)	2363(13)	1872(9)	93(6)
C(11C)	-1985(12)	5048(14)	1891(9)	97(7)
C(12)	4153(3)	2360(4)	2085(2)	47(1)
C(13)	3853(3)	2684(5)	2712(2)	58(1)
C(14)	4421(4)	3322(5)	3303(3)	75(2)
C(15)	5283(4)	3664(5)	3274(3)	77(2)
C(16)	5587(4)	3377(6)	2650(4)	91(2)
C(17)	5027(4)	2706(5)	2075(3)	67(2)
C(18)	3760(3)	1763(5)	396(2)	52(1)
C(19)	4080(4)	3074(6)	235(3)	87(2)
C(20)	4410(5)	3288(7)	-379(4)	109(2)
C(21)	4411(4)	2217(9)	-859(3)	97(2)
C(22)	4079(6)	943(8)	-728(4)	133(3)
C(23)	3769(4)	697(6)	-96(3)	99(2)
C(24)	3347(3)	-650(5)	1475(2)	52(1)
C(25)	3956(3)	-1252(5)	2048(2)	61(1)
C(26)	3997(4)	-2726(7)	2178(3)	83(2)
C(27)	3419(5)	-3645(6)	1724(4)	92(2)
C(28)	2815(5)	-3081(6)	1163(4)	87(2)
C(29)	2763(4)	-1602(5)	1027(3)	66(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

One of the methylene protons in (1 R = Me) shows a small coupling, $J_{(\text{H}-\text{H})} = 0.6$ Hz, with protons of the methyl group.

All compounds (1) are solids, with melting points above 100°C. A DSC experiment with (1 R = C₆H₄¹Bu-p), conducted between 25 and 180°C, indicated that the material melted cleanly at 159°C, but that no crystallisation occurred on cooling. Instead the material remained as a glassy substance. On reheating the glassy sample from 60°C, an exothermic transition occurred at ca. 110°C (a possible cold crystallisation), followed by two endothermic processes (both possibly fusions), with maxima at ca. 135 and 150°C. Maintaining (1 R = Me or C₆H₄Me-p) without solvent at 170°C for 30 min in air clearly resulted in extensive decomposition: (1 R = Me) was more readily decomposed. The

^1H NMR spectra of the resulting viscous oils in CDCl_3 were complexed and indicated the decomposition of the germanium sulphoxides and, in each case, the formation of several products. The thermal reaction of $\text{R}_3\text{SiCHR}^2\text{S(O)R}$ is a Pummerer-type rearrangement and provides an *O*-triorganosilyl hemithioacetal $\text{R}_3\text{SiO-CHR}^2\text{SR}$ [3–5]. The ^1H NMR spectra of several $\text{R}_3\text{SiOCHR}^2\text{SR}$ compounds (**2**) have been reported [5,17]. Values of $\delta \text{H(CHO)}$ for (**2** $\text{R}^2 = \text{Ph}$) and (**2** $\text{R} = \text{alkyl}$) are ca. 6.0–6.3 and 5.1–5.4 ppm respectively: for $\text{Ph}_3\text{GeOCH}_2\text{SR}$, the $\delta \text{H(CH}_2\text{O)}$ values anticipated would be ca. 4.2–4.5 ppm. However, no major absorptions in this area were detected in the ^1H NMR spectra and it has to be concluded that $\text{Ph}_3\text{GeOCH}_2\text{SR}$ compounds do not feature significantly among the products of thermolysis of (**1**).

3.1. Crystal structure of (**1** $\text{R} = \text{C}_6\text{H}_4^i\text{Bu-}p$)

Colourless crystals suitable for an X-ray crystallography study were obtained for (**1** $\text{R} = \text{C}_6\text{H}_4^i\text{Bu-}p$). The atom arrangement and numbering system for (**1** $\text{R} = \text{C}_6\text{H}_4^i\text{Bu-}p$) are shown in Fig. 1. The atom coordinates are listed in Table 2; selected bond angles and lengths are in Table 3. The geometry about germanium is essentially tetrahedral with the range of valency angles at germanium from 106.1(2) to 112.2(2)°. The $\text{Ge-C}_{\text{aryl}}$ bond lengths are between 1.932(5) and 1.942(5) Å, with the $\text{Ge-C}_{\text{alkyl}}$ bond length equal to 1.963(5) Å: all are within the expected ranges. The Newman projection about the C(1)-S bond is shown in Fig. 2. The torsional angles Ge-C(1)-S-O and Ge-C(1)-S-C(2) are 62.3(3)° and 171.7(2)° respectively. The $\text{Ge} \cdots \text{O}$ separation is 3.410(4) Å.

As measured by the dihedral angle between the planes, $[\text{C(2)-C(7)}]$ and $[\text{O,S,C(2)}]$, the S-O bond is

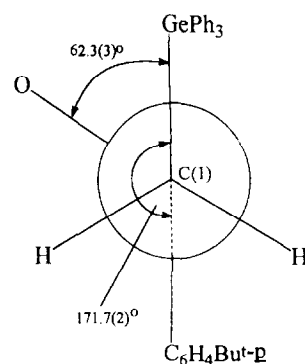


Fig. 2. Group arrangement about the central C(1)-S bond in (**1** $\text{R} = \text{C}_6\text{H}_4^i\text{Bu-}p$).

twisted by 7.0(3)° from coplanarity with the tert-butylphenyl ring. The corresponding twist angles in the methyl aryl sulphoxides $\text{MeS(O)C}_6\text{H}_4\text{Me-}p$ [18], $\text{MeS(O)C}_6\text{H}_3\text{F}_2\text{-3,4}$ and $\text{MeS(O)C}_6\text{H}_3\text{F}_2\text{-3,5}$ [19] are also small, being between 1.9(4) and 14.8(6)°. The non-planarity of the S(O) and attached aryl ring is in agreement with an M.O. calculation, from which it was concluded that the minimum in the energy profile for rotation about the $\text{C}_{\text{Ar}}\text{-S}$ bond corresponds to a twist angle of 7.3° between the S=O bond and the plane of the aryl ring [20]. The tert-butyl group is disordered with each of its methyl carbon atoms occupying one of three positions of equal occupancy at 20°C.

Acknowledgements

The use of the EPSRC X-ray crystallographic service at the University of Wales, Cardiff is gratefully acknowledged. Mr. B. Patterson is thanked for obtaining the DSC data.

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Table 3

Selected bond lengths (Å) and angles (°)

Ge-C(24)	1.932(5)		
Ge-C(18)	1.933(4)		
Ge-C(12)	1.942(5)		
Ge-C(1)	1.963(5)		
S-O	1.501(3)		
S-C(1)	1.777(4)		
S-C(2)	1.796(5)		
C(24)-Ge-C(18)	110.2(2)	C(3)-C(2)-S	119.8(4)
C(24)-Ge-C(12)	108.8(2)	C(7)-C(2)-S	120.8(4)
C(18)-Ge-C(12)	110.2(2)		
C(24)-Ge-C(1)	109.2(2)	C(17)-C(12)-Ge	122.6(4)
C(18)-Ge-C(1)	112.2(2)	C(13)-C(12)-Ge	120.3(4)
C(12)-Ge-C(1)	106.1(2)		
O-S-C(1)	103.7(2)	C(25)-C(24)-Ge	120.8(4)
O-S-C(2)	106.8(2)	C(29)-C(24)-Ge	122.0(4)
C(1)-S-C(2)	97.9(2)	C(23)-C(18)-Ge	121.8(4)
S-C(1)-Ge	114.8(2)	C(19)-C(18)-Ge	122.6(4)

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