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Synthesis of 1-Triphenylgermylpropiono-4-substituted Semicarbazides, Thiosemicarbazides and Their Heterocyclic Derivatives

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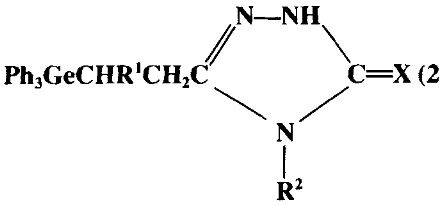
Twenty-one new organogermanium compounds with the formulae $Ph_3GeCHR^1CH_2CONHNHC(X)NHR^2$ (1) ($R^1=H$, Ph; $R^2=Ph$, p-CH_3Ph, o-CH_3Ph, p-ClPh, COPh, $X=S$, O) and



(2)

($R^1=H$, Ph; $R^2=Ph$, p-CH_3Ph, o-CH_3Ph, p-ClPh; $X=S$, O) were synthesized and characterized by elemental analysis, ^1H NMR, IR, MS and X-ray diffraction techniques. Compounds 1 were prepared by the reactions of $Ph_3GeCHR^1CH_2CONHNH_2$ with R^2NCX in chloroform in 77–94% yields, and 2 were obtained by refluxing 1 with sodium hydroxide (8%) with yields of 55–94%.

Keywords: organogermanium; semicarbazide; thiosemicarbazide; triazoline; synthesis; structure

INTRODUCTION

Various 1-acyl-4-substituted thiosemicarbazide derivatives are known to possess biological properties such as antitubercular,[1] antifungal,[1,2] hypoglycemic[3] and antibacterial[4] activities. Even the cyclic compounds like oxadiazoles, thiadiazoles and mercaptotriazoles derived from these thiosemicarbazides have also been widely reported to exhibit antitubercular,[5] bacteriostatic,[6] hypoglycemic,[7,8] diuretic,[9] antiviral[10] and antifungal[11] effects. Trialkylgermylpropanoic acid derivatives can selectively inhibit the decomposition of some enzymes[12] and some of them show antibacterial[13] and antifungal[14] effects. In order to take advantage of the organogermanium compounds, thiosemicarbazides and the heterocycles, we synthesized a series of compounds **1** and **2** according to Eqns [1]–[4], with some semicarbazides and their heterocyclic derivatives involved for comparison.

$$Ph_3GeCHR^1CH_2COOH + HOEt \rightarrow Ph_3GeCHR^1CH_2COOEt + H_2O \quad [1]$$

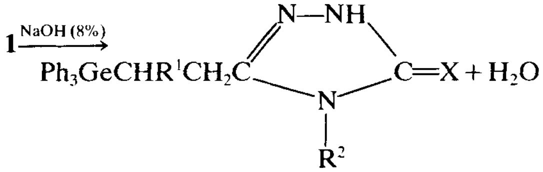
$R^1=H$, **3a** $\qquad R^1=H$, **4a**
$R^1=Ph$, **3b** $\qquad R^1=Ph$, **4b**

$$\mathbf{4a(4b)} + H_2NNH_2 \rightarrow Ph_3GeCHR^1CH_2CONHNH_2 + HOEt \quad [2]$$

$R^1=H$, **5a**
$R^1=Ph$, **5b**

$$\mathbf{5a(5b)} + R^2NCX \rightarrow Ph_3Ge\overset{1}{C}HR^1\overset{2}{C}H_2CONHNHC(X)NHR^2 \quad [3]$$

1(6a–6l)



[4]

2(7a–7l)

where $R^1=H$, $X=S$

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R^2 = Ph (**6a**, **7a**), *p*-ClPh(**6b**, **7b**), *p*-CH_3Ph (**6c**, **7c**), *o*-CH_3Ph (**6d**, **7d**), COPh (**6e**)
R^1 = H, X = O, R^2 = Ph (**6f**, **7f**)
R^1 = Ph, X = S
R^2 = Ph (**6g**, **7g**), *p*-ClPh (**6h**), *p*-CH_3Ph(**6i**, **7i**), *o*-CH_3Ph (**6j**, **7j**), COPh (**6k**)
R^1 = Ph, X = O, R^2 = Ph (**6l**, **7l**)

These compounds expected to possess better antibacterial, antifungal and antiviral activities, were characterized by elemental analysis, IR, ^1H NMR, MS and X-ray diffraction techniques.

EXPERIMENTAL

IR spectra were recorded on a Shimadzu IR-435 spectrometer in KBr discs. ^1H NMR spectra were measured on a Bruker Ac-200 spectrometer in $CDCl_3$ or DMSO-d_6 with TMS as internal standard. Mass spectra were recorded on an HP-5988A at 70 eV. The ionization temperature was 200 °C. Elemental analyses were determined on an MT-3 elemental analyzer. Melting points were obtained on a Thomas Hoover capillary melting-point apparatus and uncorrected.

A colorless crystal of compound **7g** with dimensions of 0.3 mm × 0.3 mm × 0.4 mm was selected and used for the X-ray analysis. The reflections in the range of $4° < 2\theta < 46°$ were collected on an ENRAF–Nonius CAD 4 X-ray diffractiometer with Mo Kα radiation ($\lambda = 0.71073$ Å), where $\omega/2\theta$ techniques were employed at 299(1) K. Among 3810 independent reflections 2709 observed reflections [$I \geqslant 3\sigma(I)$] were selected and used for the refinement. The LP factors were applied to the data. The structure was solved by a direct method (Multan 82) and refined by the full matrix least-squares technique with anisotropic temperature factors for all non-hydrogen atoms. All calculations were performed on a PDP 11/44 computer using the SDP-PLUS program system.

Triphenylgermylpropanoic acids (3a, 3b)

Compounds **3a** and **3b** were synthesized according to Ref. 15.

3a: m.p. 134–136 °C, yield 52%. Analysis: Found (%): C, 66.39; H, 5.23. Calcd. (%): C, 66.91; H, 5.35.

3b: m.p. 193–195 °C; yield 70%. Analysis: Found (%): C, 71.46; H, 5.61; Calcd. (%): C, 71.57; H, 5.34.

Table 1 Yields and elemental analyses of compounds **6** and **7**

Compound	Formula	Yield (%)	M.p. (°C)	Elemental Analysis (%): Found (Calcd.) C	H	N
6a	$C_{28}H_{27}GeN_3OS$	85.1	173–175	63.57 (63.91)	5.09 (5.17)	7.84 (7.99)
6b	$C_{28}H_{26}ClGeN_3OS$	79.4	165–168	59.84 (59.98)	4.40 (4.67)	6.69 (7.49)
6c	$C_{29}H_{29}GeN_3OS$	77.8	175–178	64.68 (64.47)	5.79 (5.41)	7.57 (7.78)
6d	$C_{29}H_{29}GeN_3OS$	83.8	164–166	64.73 (64.47)	5.53 (5.41)	7.80 (7.78)
6e	$C_{29}H_{27}GeN_3O_2S$	94.0	176–178	62.74 (62.84)	4.85 (4.91)	7.30 (7.58)
6f	$C_{27}H_{28}GeN_3O_2$	79.8	198–200	65.68 (65.92)	5.19 (5.33)	8.38 (8.24)
6g	$C_{34}H_{31}GeN_3OS$	89.1	176–178	67.83 (67.80)	5.44 (5.19)	6.88 (6.98)
6h	$C_{34}H_{30}ClGeN_3OS$	93.3	172–174	63.96 (64.13)	5.08 (4.75)	6.72 (6.60)
6i	$C_{35}H_{33}GeN_3OS$	94.3	178–181	68.39 (68.20)	5.66 (5.40)	6.62 (6.82)
6j	$C_{35}H_{33}GeN_3OS$	87.7	177–179	68.39 (68.20)	5.74 (5.40)	6.69 (6.82)
6k	$C_{35}H_{31}GeN_3O_2S$	81.2	160–163	66.66 (66.69)	5.10 (4.96)	6.73 (6.67)
6l	$C_{34}H_{31}GeN_3O_2$	87.1	194–196	69.48 (69.66)	5.26 (5.33)	7.19 (7.17)
7a	$C_{28}H_{25}GeN_3S$	71.4	233–236	66.16 (66.18)	5.12 (4.96)	8.06 (8.27)
7b	$C_{28}H_{24}ClGeN_3S$	72.1	278–281^b	61.87 (61.97)	4.63 (4.46)	7.79 (7.74)
7c	$C_{29}H_{27}GeN_3S$	77.6	268–271^b	66.41 (66.70)	4.82 (5.21)	7.83 (8.05)
7d	$C_{29}H_{27}GeN_3S^a$	94.0	230–232	66.78 (66.70)	5.29 (5.21)	8.08 (8.05)
7f	$C_{28}H_{25}GeN_3O$	92.3	198–201	68.22 (68.33)	5.10 (5.12)	8.22 (8.54)
7g	$C_{34}H_{29}GeN_3S^a$	94.3	236–238	69.63 (69.89)	5.14 (5.00)	7.13 (7.19)
7i	$C_{35}H_{31}GeN_3S^a$	65.2	224–226	69.47 (70.26)	5.01 (5.22)	6.43 (7.02)
7j	$C_{35}H_{31}GeN_3S$	55.2	180–182	69.77 (70.26)	4.85 (5.22)	6.85 (7.02)
7l	$C_{34}H_{29}GeN_3O^a$	70.1	235–237	71.61 (71.87)	5.29 (5.14)	7.10 (7.39)

^{a} Crystals; the others are powders. ^{b} Decomposed.

Table 2 ^{1}H NMR and IR data of compounds **6** and **7**

Compound	^{1}H NMR data δ (ppm)	IR data (cm^{-1})
6a	9.42 (s, 1H, NHPh), 8.94 (s, 1H, NHCS), 8.51 (s, 1H, CONH), 7.21–7.46 (m, 20H, Ph), 2.42 (t, $^3J_{HH}$ = 8.53 Hz, 2H, CH$_2$CO), 1.81 (t, $^3J_{HH}$ = 8.53 Hz, 2H, GeCH$_2$)	3195, 3330 (NH); 1661 (C=O); 1192 (C=S); 610 (Ge—C)
6b	9.85 (s, 1H, NHPh), 9.58 (s, 1H, NHCS), 7.80 (b, 1H, CONH), 7.30–7.50 (m, 19H, Ph), 2.30 (t, $^3J_{HH}$ = 8.50 Hz, 2H, CH$_2$CO), 1.76 (t, $^3J_{HH}$ = 8.50 Hz, 2H, GeCH$_2$)	3263, 3388(NH); 1670 (C=O); 1198 (C=S); 598 (Ge—C)
6c	8.64–9.44 (b, 3H, NH), 7.10–7.45 (m, 19H, Ph), 2.45 (t, $^3J_{HH}$ = 8.50 Hz, 2H, CH$_2$CO), 2.31 (s, 3H, CH$_3$), 1.79 (t, $^3J_{HH}$ = 8.50 Hz, 2H, GeCH$_2$)	3224, 3361 (NH); 1682 (C=O); 1181 (C=S); 608 (Ge—C)
6d	8.20–9.30 (b, 3H, NH), 7.23–7.44 (m, 19H, Ph), 2.43 (t, $^3J_{HH}$ = 8.43 Hz, 2H, CH$_2$CO), 2.24 (s, 3H, CH$_3$), 1.79 (t, $^3J_{HH}$ = 8.43 Hz, 2H, GeCH$_2$)	3139, 3315 (NH); 1666 (C=O); 1195 (C=S); 592 (Ge—C)
6e	13.12 (s, 1H, CSNH), 9.06 (s, 1H, NHCS), 8.91 (s, 1H, CONH), 7.38–7.88 (m, 20H, Ph), 2.51 (t, $^3J_{HH}$ = 8.64 Hz, 2H, CH$_2$CO), 1.91 (t, $^3J_{HH}$ = 8.64 Hz, 2H, GeCH$_2$)	3265, 3373 (NH); 1666, 1635 (C=O); 1162 (C=S); 580 (Ge—C)
6f	9.59 (s, 1H, NHPh), 8.68 (s, 1H, NHCO), 7.92 (s, 1H, CONH), 6.90–7.44 (m, 20H, Ph), 2.28 (t, $^3J_{HH}$ = 8.74 Hz, 2H, CH$_2$CO) 1.77 (t, $^3J_{HH}$ = 8.74 Hz, 2H, GeCH$_2$)	3262, 3387 (NH); 1670 (C=O); 589 (Ge—C)
6g	8.00–9.15 (b, 3H, NH), 6.93–7.74 (m, 25H, Ph), 3.73 (t, $^3J_{HH}$ = 7.35 Hz, 1H, CH), 2.96 (d, $^3J_{HH}$ = 7.35 Hz, 2H, CH$_2$)	3220, 3398(NH); 1678 (C=O); 1234 (C=S); 600 (Ge—C)
6h	7.95–9.20 (b, 3H, NH), 6.95–7.46 (m, 24H, Ph), 3.71 (t, $^3J_{HH}$ = 7.35 Hz, 1H, CH), 2.98 (d, $^3J_{HH}$ = 7.35 Hz, 2H, CH$_2$)	3218, 3390 (NH); 1666 (C=O) 1204 (C=S); 606 (Ge—C)
6i	8.82 (b, 1H, NHCS), 8.57 (b, 1H, NHPH), 7.74 (b, 1H, CONH), 6.87–7.34 (m, 24H, Ph), 3.61–3.64 (m, 1H, CH), 2.86–2.89 (m, 2H, CH$_2$), 2.30 (s, 3H, CH$_3$)	3200, 3361 (NH); 1662 (C=O) 1207 (C=S); 600 (Ge—C)
6j	8.50–8.75 (b, 3H, NH), 6.87–7.38 (m, 24H, Ph), 3.62–3.66 (m, 1H, CH), 2.86–2.88 (m, 2H, CH$_2$), 2.05 (s, 3H, CH$_3$)	3200, 3372 (NH); 1661 (C=O); 1212 (C=S); 600 (Ge—C)
6k	13.12 (s, 1H, CSNH), 9.01 (s, 1H, NHCS), 8.89 (s, 1H, CONH), 7.05–7.90 (m, 25H, Ph), 3.89 (m, 1H, CH), 3.10 (m, 2H, CH$_2$)	3211, 3385 (NH); 1661 (C=O); 1167 (C=S)
6l	9.62 (s, 1H, NHPh). 8.38 (s, 1H, NHCO), 7.90 (s, 1H, CONH), 6.96–7.41 (m, 25H, Ph), 3.82–3.86 (m, 1H, CH), 2.63–3.02 (m, 2H, CH$_2$)	3200, 3364 (NH); 1637 (C=O); 600 (Ge—C)
7a	11.13 (b, 1H, NH), 7.32–7.55 (m, 20H, Ph), 2.63 (t, $^3J_{HH}$ = 8.40 Hz, 2H, CH$_2$CN), 1.70 (t, $^3J_{HH}$ = 8.40 Hz, 2H, GeCH$_2$)	3379 (NH); 1425, 1490, 1580 (C=C, C=N); 1305 (C=S); 616 (Ge—C)
7b	7.20–7.44 (m, 19H, Ph), 2.60–2.80 (m, 2H, CH$_2$CN), 1.71–1.73 (m, 2H, GeCH$_2$)	3383 (NH); 1426, 1480, 1562 (C=C, C=N); 1300 (C=S); 617 (Ge—C)
7c	7.07–7.38 (m, 19H, Ph), 2.68 (t, $^3J_{HH}$ = 8.54 Hz, 2H, CH$_2$CN), 2.46 (s, 3H:, CH$_3$), 1.75 (t, $^3J_{HH}$ = 8.54 Hz, 2H, GeCH$_2$)	3401 (NH); 1424, 1490, 1562 (C=C, C=N); 1309 (C=S); 613 (Ge—C)
7d	7.17–7.60 (m, 19H, Ph), 2.60–2.72 (m, 2H, CH$_2$CN), 2.16 (s, 3H, CH$_3$), 1.75–1.85 (m, 2H, GeCH$_2$)	3382 (NH); 1424, 1488, 1562 (C=C, C=N); 1304 (C=S); 615 (Ge—C)
7f	9.50 (b, 1H, NH), 7.16–7.49 (m, 20H, Ph), 2.65 (t, $^3J_{HH}$ = 8.48 Hz, 2H, CH$_2$CN), 1.67 (t, $^3J_{HH}$ = 8.48 Hz, 2H, GeCH$_2$)	3374 (NH); 1413, 1514, 1571 (C=C, C=N); 1690 (C=O); 609 (Ge—C)
7g	11.10 (b, 1H, NH), 6.72–7.62 (m, 25H, Ph), 3.10–3.25 (m, 3H, CH, CH$_2$)	3387 (NH); 1435, 1480, 1560 (C=C, C=N); 1325 (C=S)
7i	10.85 (b, 1H, NH), 7.05–7.40 (m, 24H, Ph), 3.10–3.20 (m, 3H, CH, CH$_2$), 2.53 (s, 3H, CH$_3$)	3389 (NH); 1425, 1480, 1560 (C=C, C=N); 1325 (C=S)
7j	7.03–7.50 (m, 24H, Ph), 3.10–3.20 (m, 3H, CH, CH$_2$), 2.09 (s, 3H, CH$_3$)	3390 (NH); 1426, 1480, 1560 (C=C, C=N); 1329 (C=S)
7l	11.38 (s, 1H, NH), 6.71–7.60 (m, 25H, Ph), 2.95–3.16 (m, 3H, CH, CH$_2$)	3381 (NH); 1415, 1481, 1563 (C=C, C=N); 1696 (C=O); 598 (Ge—C)

Triphenylgermylpropionates (4a, 4b)

4a, **3a** (0.5 g) was refluxed with absolute alcohol (10 ml) for 8.5 h. After the removal of most of the solvent, **4a** crystallized out with 89.4% yield, m.p. 59–61 °C. Analysis: Found (%): C, 67.57; H, 5.93; Calcd. (%): C, 68.20; H, 5.97. ^{1}H NMR (δ

in $CDCl_3$): 7.37–7.52 (m, 15H, Ph), 4.04 (q, $^3J_{HH}=7.13$ Hz, 2H, OCH_2), 2.49 (t, $^3J_{HH}=8.58$ Hz, 2H, CH_2CO), 1.83 (t, $^3J_{HH}=8.58$ Hz, 2H, $GeCH_2$), 1.18 (t, $^3J_{HH}=7.13$ Hz, 3H, CH_3).

Compound **4b** was prepared by esterification of **3b** with alcohol using conc. sulphuric acid as a catalyst; it was obtained in 81.7% yield, m.p. 98–101 °C. Analysis: Found (%): C, 72.20; H, 5.80; Calcd. (%): C, 72.39, H, 5.87. ^1H NMR (δ in $CDCl_3$): 6.97–7.37 (m, 20 H, Ph), 3.88 (q, $^3J_{HH}=7.14$ Hz, 2H, OCH_2), 3.70 (t, $^3J_{HH}=7.81$ Hz, 1H, CH), 2.96 (d, $^3J_{HH}=7.81$ Hz, 2H, CH_2CO), 1.03 (t, $^3J_{HH}=7.14$ Hz, 3H, CH_3).

Triphenylgermylpropionohydrazides (5a, 5b)

Compound **5a** was prepared as follows: **4a** (0.70 g) was refluxed with 85% hydrazine in water (15 ml) for 5.5 h. The reaction mixture was cooled to room temperature, and the precipitate was filtered and washed with water three times and ethyl ether three times. The product **5a** was recrystallized from a mixture of chloroform and petroleum ether as 0.60 g needlelike crystals in 88.8% yield, m.p. 179–181 °C. Analyis: Found (%): C, 64.07; H, 5.55; N, 7.23; Calcd (%): C, 64.50; H, 5.67; N, 7.16, ^1H NMR (δ in $CDCl_3$): 7.34–7.50 (m, 15H, Ph), 6.53 (b, 1H, CONH), 3.75 (b, 2H, NH_2), 2.29 (t, $^3J_{HH}=8.48$ Hz, 2H, CH_2CO), 1.85 (t, $^3J_{HH}=8.48$ Hz, 2H, $GeCH_2$).

Compound **5b** was prepared from **4b** by the same method as above in 93.5% yield, m.p. 186–188 °C. Analysis: Found (%): C, 69.05; H, 5.97; N, 5.95; Calcd. (%): C, 69.42; H, 5.61; N, 6.00. ^1H NMR (δ in $CDCl_3$): 6.81–7.34 (m, 20H, Ph), 4.49 (b, 3H, NH, NH_2), 3.69 (m, 1H, CH), 2.83 (m, 2H, CH_2).

1-Triphenylgermylpropiono-4-phenyl thiosemicarbazides and some semicarbazides (1)

Compound **5a** or **5b** (1 g) and equimolar isocyanate or isothiocyanate were added to dry chloroform (40 ml) and refluxed for 3 h. The mixture was filtered and petroleum ether was added to the filtrate. The products precipitated were recrystallized from chloroform–petroleum ether.

1-Triphenylgermylpropiono-4-benzoyl thiosemicarbazide (6e)

The reaction of benzyl chloride (0.43 g) with potassium thiocyanate (0.48 g) in dry acetonitrile (40 ml) was carried out for 2 h at room temperature with stirring. The mixture was filtered and **5a** (1.10 g) was added and refluxed for 2 h. After removal of the solvent, the product was recrystallized from the mixed solvent of chloroform and petroleum ether.

In the same way, **6k** was prepared.

3-(Triphenylgermyl)ethyl-4-substituted-Δ^2-1,2,4-triazoline-5-thiones and the corresponding derivatives of semicarbazides (2)

The thiosemicarbazide or semicarbazide **1** (0.5 g) was dissolved in sodium hydroxide (8%, 20 ml) and refluxed for 3 h. The resulting solution was cooled and filtered. The filtrate was acidified with dilute hydrochloric acid and the precipitated solid filtered off after cooling, washed with water and recrystallized from chloroform and petroleum ether.

RESULTS AND DISCUSSION

Yields and elemental analyses of the compounds are listed in Table 1. The thiosemicarbazides and

Table 3 MS data of **7a**, **7j** and **6a**

7a			**7j**			**6a**		
m/z	Fragment	Intensity	*m/z*	Fragment	Intensity	*m/z*	Fragment	Intensity
509	M^+	3	599	M^+	15	305	Ph_3Ge^+	21
432	M^+—Ph	39	522	M^+—Ph	4	228	Ph_2Ge^+	3
305	Ph_3Ge^+	59	305	Ph_3Ge^+	100	151	$PhGe^+$	34
228	Ph_2Ge^+	6	228	Ph_2Ge^+	10	77	Ph^+	100
151	$PhGe^+$	66	151	$PhGe^+$	20			
77	Ph^+	100	91	$PhCH_2^+$	13			

Table 4 Atomic coordinates and thermal parameters for **7g**

Atom	x	y	z	B_{eq} (Å^2)[a]
Ge	0.1477(1)	0.35685(8)	0.37836(7)	3.28(2)
S	0.2871(3)	0.0745(2)	−0.0370(2)	4.89(6)
C(1)	0.2426(9)	0.3083(7)	0.2639(6)	3.7(2)
C(2)	0.265(1)	0.1644(7)	0.3061(6)	4.2(2)
C(11)	0.1098(9)	0.5325(7)	0.3065(6)	3.6(2)
C(12)	0.221(1)	0.6228(8)	0.2624(7)	4.9(2)
C(13)	0.192(1)	0.7456(8)	0.1953(7)	5.7(3)
C(14)	0.057(1)	0.7793(8)	0.1714(7)	6.2(3)
C(15)	−0.051(1)	0.6932(9)	0.2174(8)	6.5(3)
C(16)	−0.022(1)	0.5704(8)	0.2842(7)	4.9(2)
C(21)	0.2564(8)	0.3210(7)	0.4938(6)	3.5(2)
C(22)	0.306(1)	0.4192(9)	0.5166(7)	5.7(2)
C(23)	0.387(1)	0.388(1)	0.6017(8)	7.3(3)
C(24)	0.418(1)	0.265(1)	0.6623(8)	7.6(4)
C(25)	0.367(1)	0.169(1)	0.6389(8)	7.1(4)
C(26)	0.287(1)	0.1980(9)	0.5538(7)	4.8(2)
C(31)	−0.0281(9)	0.2649(7)	0.4314(6)	3.9(2)
C(32)	−0.088(1)	0.2437(8)	0.5347(7)	4.9(2)
C(33)	−0.220(1)	0.1845(9)	0.5693(8)	6.2(3)
C(34)	−0.289(1)	0.1457(9)	0.5064(8)	5.8(3)
C(35)	−0.230(1)	0.1646(9)	0.4035(8)	5.8(3)
C(36)	−0.0982(9)	0.2257(8)	0.3673(7)	4.8(2)
C(41)	0.3765(9)	0.3865(7)	0.2194(6)	4.2(2)
C(42)	0.494(1)	0.3599(9)	0.2704(8)	5.6(3)
C(43)	0.612(1)	0.442(1)	0.2299(9)	8.1(3)
C(44)	0.604(1)	0.548(1)	0.1391(9)	8.5(4)
C(45)	0.490(1)	0.577(1)	0.0860(9)	8.6(4)
C(46)	0.371(1)	0.4913(9)	0.1249(7)	6.5(3)
C(51)	0.1031(9)	0.1646(7)	0.1245(6)	3.9(2)
C(52)	0.001(1)	0.0736(8)	0.1827(7)	5.9(2)
C(53)	−0.137(1)	0.108(1)	0.1687(8)	7.5(3)
C(54)	−0.172(1)	0.226(1)	0.1036(8)	8.6(3)
C(55)	−0.066(1)	0.317(1)	0.0455(8)	7.4(3)
C(56)	0.071(1)	0.2837(9)	0.0584(7)	5.3(3)
C(61)	0.3215(9)	0.1292(7)	0.2136(6)	3.6(2)
N(62)	0.4459(8)	0.0882(6)	0.2040(5)	4.4(2)
N(63)	0.4486(7)	0.0662(6)	0.1116(5)	4.1(2)
C(64)	0.3316(9)	0.0910(7)	0.0700(6)	3.6(2)
N(65)	0.2457(7)	0.1338(6)	0.1351(5)	3.5(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$$B_{eq}=\frac{4}{3}[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab\cdot\cos\gamma\cdot\beta_{12}+ac\cdot\cos\beta\cdot\beta_{13}+bc\cdot\cos\alpha\cdot\beta_{23}]$$

$$\beta=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$$

semicarbazides are all in white powder form, while five heterocycles among the nine are colorless crystals. Most of the compounds are soluble in chloroform and tetrahydrofuran.

^{1}H NMR and IR data are shown in Table 2. The chemical shifts of ^{1}H in NH for type **1** compounds are in the range of 7.74–9.85 ppm except those of compounds **6e** and **6k**. The protons of C_1 and C_2 are magnetically equivalent, respectively, when $R^1=H$, and the two protons of C_2 become nonequivalent for most of the compounds with $R^1=Ph$. The chemical shifts of protons in NH for type **2** compounds appear around 11.00 ppm. Some of the corresponding peaks were not observed for the same types of compounds, which may be caused by the exchange between deuteriums and the active protons.

The absorbance of stretching vibration of C=S for type **1** compounds are around 1200 cm^{-1} (m) and Ge—C (alkyl) around 600 cm^{-1} (w)[16] (Table 2). No C=O peaks were observed in IR spectra for type **2** compounds except those of compounds **7f** and **7l**. The C=S absorbance of the heterocycles **2** shift about 100 cm^{-1} to the near-infrared region from the absorbance of **1**.

Some MS data of compounds **6a**, **7a** and **7j** are shown in Table 3. No molecular ion peaks were observed for the thiosemicarbazide **6a**. The two heterocycles are stable and their molecular ion peaks were all detected. All three compounds have the fragments of Ph_3Ge^+, Ph_2Ge^+ and $PhGe^+$ in their mass spectra.

The crystal structure of compound **7g** was determined by single-crystal X-ray diffraction. The crystal is triclinic with space group $P\bar{1}$, $a=9.772(3)$ Å, $b=11.643(3)$ Å, $c=13.960(3)$ Å; $\alpha=66.55(2)°$, $\beta=83.49(2)°$, $\gamma=88.49(2)°$, $Z=2$, $V=1440.0(8)$ Å^3, $M_r=584.28$, $F(000)=604$, $\mu(\text{Mo K}\alpha)=114.4$ mm^{-1}, $D_c=1.349$ g ml^{-1}, $R=0.058$, $R_w=0.068$.

Table 4 presents the coordinates of nonhydrogen atoms and isotropic thermal parameters. Selected bond lengths and bond angles are listed in Tables 5 and 6, respectively. The structure of **7g** is shown in Fig. 1. The bond lengths of N(63)–C(64), C(64)–N(65) and C(64)–S (1.310, 1.393 and 1.684 Å) are close to the corresponding ones (1.33, 1.33 and 1.7 Å) in

Table 5 Selected bond distances (Å) in **7g**

Ge–C(1)	2.020(5)[a]	C(2)–C(61)	1.545(8)
Ge–C(11)	1.933(6)	C(51)–N(65)	1.432(8)
Ge–C(21)	1.927(6)	C(61)–N(62)	1.301(8)
Ge–C(31)	1.948(6)	C(61)–N(65)	1.372(8)
S–C(64)	1.684(6)	N(62)–N(63)	1.408(7)
C(1)–C(2)	1.558(8)	N(63)–C(64)	1.310(8)
C(1)–C(41)	1.529(8)	C(64)–N(65)	1.393(8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 6 Selected bond angles (deg) in **7g**

C(1)-Ge-C(11)	104.1(2)[a]	N(62)-C(61)-N(65)	112.9(5)
C(1)-Ge-C(21)	112.8(2)	C(61)-N(62)-N(63)	102.6(5)
C(1)-Ge-C(31)	108.6(3)	N(62)-N(63)-C(64)	113.4(5)
C(11)-Ge-C(21)	113.9(3)	S-C(64)-N(63)	129.6(5)
C(11)-Ge-C(31)	108.4(3)	Ge-C(31)-C(32)	118.9(5)
C(21)-Ge-C(31)	108.8(3)	Ge-C(31)-C(36)	120.9(5)
Ge-C(1)-C(2)	110.8(4)	C(1)-C(41)-C(42)	122.7(6)
Ge-C(1)-C(41)	107.8(4)	C(1)-C(41)-C(46)	115.5(7)
C(2)-C(1)-C(41)	113.6(5)	C(52)-C(51)-N(65)	119.0(7)
C(1)-C(2)-C(61)	109.1(5)	C(56)-C(51)-N(65)	118.8(7)
Ge-C(11)-C(12)	120.5(6)	S-C(64)-N(65)	125.5(5)
Ge-C(11)-C(16)	120.3(6)	N(63)-C(64)-N(65)	105.0(6)
Ge-C(21)-C(22)	120.4(5)	C(51)-N(65)-C(61)	128.4(5)
Ge-C(21)-C(26)	119.5(6)	C(51)-N(65)-C(64)	125.1(6)
C(2)-C(61)-N(62)	123.0(6)	C(61)-N(65)-C(64)	106.2(5)
C(2)-C(61)-N(65)	124.2(5)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

thiourea.[17] Obviously, the C(64)–S bond is a double one. The sp^2-hybridized atoms forming the heterocycle, as well as S and C(51), are coplanar, with a delocalized π_6^8 bond among them except C(51). The bond lengths of C(61)–N(65), N(65)–C(64) and N(63)–C(64) fall between the single-bond C–N distance and the double-bond one. The heterocycle and the attached benzene ring are not coplanar with the dihedral angle, 96.8°, and there is no delocalized π-bond joining the two planes, so that the distance of C(51)–N(65) (1.432 Å) is approximately that of a single bond. C(61), C(2), N(62) and N(65) are nearly in the same plane, with the sum of angles N(65)–C(61)–C(2), C(2)–C(61)–N(65) and N(62)–C(61)–N(65) being 349.8° C(1), C(11), C(21) and C(31) constitute a distorted tetrahedron with Ge in the center. The average bond length between Ge and the three aromatic carbons (1.936 Å) is shorter than that between Ge and the saturated C(1) (2.020 Å), resulting from the coordination of the delocalized p-electrons in the substituted benzene rings to the Ge atom.

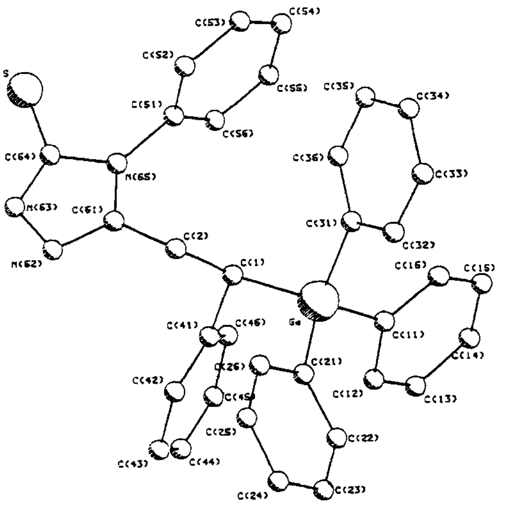

Figure 1 Structure of compound **7g**.

In summary, the result of X-ray analysis of crystal **7g** is in good agreement with those of ^1H NMR and IR. This revealed that the five-membered rings of type **2** compounds appear as triazolines, and not as the triazoles which were reported by Paul and Basu.[18]

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