

## Studies on Some New Triphenylgermanium(IV) Dithiocarbamates

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Five new triphenylgermanium(IV) dithiocarbamates of the general formula  $\text{Ph}_3\text{Ge(IV)dtc}$  (where dtc = dimethyl- or diethyl-dithiocarbamate, or morpholine-, pyrrolidine- or piperidine-N-carbodithioate) have been prepared and characterized. The spectral (IR and UV) and electric dipole moment data indicate an ester type structure of the compounds containing monodentate dithiocarbamate group. The results of TGA and DTA data have been also reported.

WE have found only a single reference<sup>1</sup> to the preparation of triethylgermanium(IV) dimethyl- and diethyl-dithiocarbamates, though in recent years several reports have appeared on the corresponding triorganotin(IV) derivatives<sup>2-4</sup>. In continuation of our previous communication<sup>5</sup> on triorganotin(IV) dithiocarbamates, we now report the preparation and characterization of five new triphenylgermanium(IV) dithiocarbamates of the general formula  $\text{Ph}_3\text{Ge(IV)dtc}$  (where dtc = dimethyl- or diethyl-dithiocarbamate, or morpholine-, pyrrolidine- or piperidine-N-carbodithioate).

### Materials and Methods

Triphenylgermanium(IV) chloride, sodium dimethyl- and diethyl-dithiocarbamates were procured from M/s Alfa Inorganics. Ammonium salts of morpholine-, pyrrolidine-, piperidine- and (N-phenyl)-piperazine-N-carbodithioate were prepared by the reported methods. Freshly distilled solvents were used after purification through the conventional methods. The germanium compounds were synthesized by the following method.

Triphenylgermanium(IV) chloride (10 mmoles) and sodium or ammonium salt of dithiocarbamic acid (12 mmoles) were taken in 30 ml of benzene. The reaction mixture was stirred for 2-3 hr and filtered. The filtrate on distilling off the excess solvent and treating with petroleum ether (60-80°) yielded a white crystalline solid which was dried *in vacuo*.

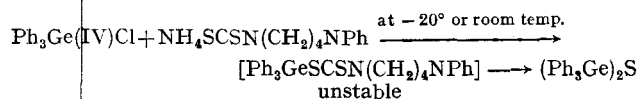
IR spectra were recorded in KBr in the region 4000-250  $\text{cm}^{-1}$  using a Perkin-Elmer 521 spectrometer. Electronic spectra of  $10^{-3}M$  solutions in chloroform were recorded with Perkin-Elmer 202 spectrometer. Molecular weights were determined cryoscopically in benzene using a Beckman thermometer of accuracy  $\pm 0.01^\circ$ . Conductance measurement of  $10^{-3}M$  solutions in nitrobenzene were made using a Philips PR 9500 conductivity bridge with a dip-type cell. Dielectric constant ( $\epsilon$ ) was measured at radio frequency of Mc/s with the help of a dipole meter type RL09. The refractive indices ( $\eta$ ) were determined with an accuracy of  $\pm 0.0002$  using an ASCO Abbe refractometer and sodium-D-line as the source of light.

### Results and Discussion

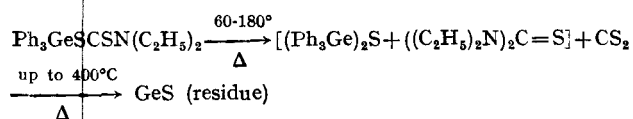
The new compounds have been prepared by metathesis between triphenylgermanium(IV) chloride and sodium or ammonium salt of dithiocarbamic acid in benzene at room temperature. While using ammonium (N-phenyl)piperazine-N-carbodithioate the reaction yields bis(triphenylgermanium) sulphide (m.p. 136-37°; lit. m.p.<sup>7</sup> 138.6°. Found: Ge, 22.12. Calc.: Ge, 22.71%) instead of the desired dithiocarbamate derivative. The probable formation of an unstable  $\text{Ph}_3\text{Ge(IV)}$  (N-phenyl)piperazine-N-carbodithioate is concluded on the basis of the known<sup>8</sup> facile decomposition of several transition and heavy metal dithiocarbamates to metal sulphide.

TABLE 1 — ANALYTICAL AND MOLECULAR WEIGHT DATA OF  $\text{Ph}_3\text{Ge(IV)dtc}$

Compound dtc	m.p. (°C)	Found (calc.), %			Molec. wt found (calc.)
		Ge	C	H	
$\text{Ph}_3\text{GeSCSN}(\text{CH}_3)_2$	109	16.23	60.92	5.50	438.9
		(16.07)	(61.07)	(5.53)	(451.6)
$\text{Ph}_3\text{GeSCSN}(\text{C}_2\text{H}_5)_2$	108-10	17.03	59.11	4.90	409.2
		(17.13)	(59.49)	(4.95)	(423.6)
$\text{Ph}_3\text{GeSCSN}(\text{CH}_2)_4\text{O}$	160-62	15.55	52.17	4.98	452.9
		(15.57)	(52.27)	(4.93)	(465.6)
$\text{Ph}_3\text{GeSCSN}(\text{CH}_2)_4$	147-48	16.02	61.25	5.00	432.0
		(16.14)	(61.38)	(5.11)	(449.6)
$\text{Ph}_3\text{GeSCSN}(\text{CH}_2)_5$	132-33	15.40	62.02	5.28	—
		(15.44)	(62.16)	(5.39)	—



The compounds are white crystalline solids with sharp melting points (Table 1). They are soluble in acetone, benzene, chloroform and nitrobenzene but are sparingly soluble in pet. ether. Molecular weight data in freezing benzene and conductance values in nitrobenzene indicate that the compounds are monomers and non-electrolytes. All the compounds are stable at ambient temperature, when freshly prepared but show signs of slow decomposition on standing at room temperature for several weeks. From the TGA data, it is indicated that the compound decomposes according to the following scheme:



The results are in agreement with the earlier reports on the analogous triorganotin(IV) (ref. 5) and organoantimony(III) derivatives<sup>9</sup>. DTA data of  $\text{Ph}_3\text{Ge(IV)}$  diethyldithiocarbamate reveal that the melting of the compound followed by its decomposition is an endothermic change. A solution of  $\text{Ph}_3\text{Ge(IV)}$  dithiocarbamates in benzene on being refluxed liberates carbon disulphide and leaves behind a solid product, identified as bis(triphenylgermanium) sulphide.

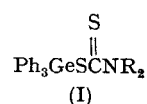
**Infrared spectra**—From a comparison of the spectra of the sodium salts of dithiocarbamic acids with those of the newly synthesized triphenylgermanium derivatives, it is apparent that the two spectra are different as far as the nature of  $\nu\text{C}-\text{N}$  and  $\nu\text{C}-\text{S}$  modes of vibrations are concerned. The  $\nu\text{C}-\text{N}$  modes in the spectra of sodium salts of dimethyldithiocarbamate<sup>11</sup>, piperidine- and morpholine<sup>12</sup>-carbodithioates, in which the ligands act as bidentate<sup>3,13,14</sup>, appear as single strong absorptions at 1485, 1465 and 1440 and the  $\nu\text{C}-\text{S}$  at 959, 965 and 990  $\text{cm}^{-1}$  respectively, while in the present organogermanium derivatives the two corresponding absorptions lie in the region 1495-1450 and 1000-959  $\text{cm}^{-1}$ . Thus there is no significant change in the position of the two absorptions but in the spectra of organogermanium derivatives both the modes of vibration undergo distinct splitting indicating an ester type structure in contrast to the presence of a chelated dithiocarbamate<sup>15</sup> group in the sodium salts where only a single absorption for the two modes of vibration is identified. Asymmetric and symmetric stretches for Ge-S and Ge-C( $\phi$ ) have been identified at  $420 \pm 1$  (ref. 16, 17),  $344 \pm 1$  and  $310 \pm 1$   $\text{cm}^{-1}$  (ref. 18-20) respectively. In triphenylgermanium chloride the asymmetric and symmetric Ge-C( $\phi$ ) stretching modes appear at 335 and 303  $\text{cm}^{-1}$  respectively<sup>21</sup> and thus do not show any significant change on being bonded to dithiocarbamate group. The strong intense absorptions at  $490 \pm 10$  and  $467 \pm 7$   $\text{cm}^{-1}$  are assigned to the out-of-plane ring bending mode<sup>17</sup>.

**Electronic spectra**—Similar to organotin(IV) dithiocarbamates<sup>2,3,5</sup> the triphenylgermanium(IV)

derivatives exhibit two absorptions at  $\approx 255$  and  $\approx 288$  nm due to intra-ligand transitions<sup>23,24</sup>. The band at  $\approx 255$  nm is suggested to be due to a  $\pi-\pi^*$  transition located mainly at the  $\text{CS}_2$  group<sup>25</sup>. Recently it has been shown that if the dithiocarbamate group is coordinated to the central metal atom with two inequivalent C-S bonds, the high energy band ( $\approx 255$  nm) has also two components<sup>26</sup>. The presence of a single intense absorption in this region supports the monodentate character of the dithiocarbamate group in the compounds.

**Electric dipole moment**—The electric dipole moment of  $\text{Ph}_3\text{Ge(IV)}$  dithiocarbamate has been calculated using Guggenheim's method<sup>27</sup>.  $\text{Ph}_3\text{GeSCSN}(\text{CH}_3)_2$ ,  $\text{Ph}_3\text{GeSCSN}(\text{C}_2\text{H}_5)_2$  and  $\text{Ph}_3\text{GeSCSN}(\text{CH}_2)_4\text{O}$  show dipole moments of 2.35, 1.67 and 2.57 D respectively. The presence of a bidentate dithiocarbamate group in triphenylgermanium(IV) dithiocarbamates is expected to give a higher dipole moment value than for a tetra-coordinated germanium(IV) compound<sup>28,29</sup>. The observed dipole moments of the compounds studied compare favourably with those of alkyl esters of dithiocarbamic acid<sup>30</sup> and may be taken as an evidence for the presence of monodentate dithiocarbamate group. A decrease in molecular dipole moment value with an increase in electron releasing ability of  $\text{NR}_2$  group (while going from R = methyl to R = ethyl) supports our conclusion on several analogous triphenyltin(IV) dithiocarbamates<sup>31</sup>.

It is concluded from the results discussed above that the triphenylgermanium(IV) dithiocarbamates possess an ester type of structure (I) similar to the corresponding triorganotin(IV) derivatives<sup>5</sup>.



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