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Di-*n*-butyldihalogermanes and Di-*n*-butylhalogenoidogermanes<sup>1</sup>

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Gradual addition of a deficiency of  $\text{Hg}(\text{CN})_2$  or  $\text{Hg}(\text{SCN})_2$  to previously known  $(n\text{-C}_4\text{H}_9)_2\text{GeH}_2$  furnishes approximately 74% yields of  $(n\text{-C}_4\text{H}_9)_2\text{GeHCN}$  or  $(n\text{-C}_4\text{H}_9)_2\text{GeHNCS}$ , respectively. These two latter compounds apparently are the first examples of the  $\text{R}_2\text{GeHX}$  type in which R is an alkyl group and X is the halogenoid CN or NCS. Very slow and gradual addition of bromine in  $\text{C}_2\text{H}_5\text{Br}$  to  $(n\text{-C}_4\text{H}_9)_2\text{GeH}_2$  furnishes a high yield of  $(n\text{-C}_4\text{H}_9)_2\text{GeBr}_2$ . Successful preparation of  $(n\text{-C}_4\text{H}_9)_2\text{Ge}(\text{NCS})_2$  uses  $[(n\text{-C}_4\text{H}_9)_2\text{GeO}]_3$  and HNCS in diethyl ether, rather than the extremely slow reaction of  $(n\text{-C}_4\text{H}_9)_2\text{GeHNCS}$  and  $\text{AgNCS}$ . Table I lists the properties and analyses of nine newly prepared compounds:  $(n\text{-C}_4\text{H}_9)_2\text{GeHNCS}$ ,  $(n\text{-C}_4\text{H}_9)_2\text{Ge}(\text{NCS})_2$ ,  $(n\text{-C}_4\text{H}_9)_2\text{GeHCN}$ ,  $(n\text{-C}_4\text{H}_9)_2\text{Ge}(\text{NCO})_2$ ,  $(n\text{-C}_4\text{H}_9)_2\text{Ge}[\text{N}(\text{CH}_3)_2]_2$ ,  $(n\text{-C}_4\text{H}_9)_2\text{GeF}_2$ ,  $(n\text{-C}_4\text{H}_9)_2\text{GeBr}_2$ ,  $(n\text{-C}_4\text{H}_9)_2\text{GeI}_2$  and  $[(n\text{-C}_4\text{H}_9)_2\text{GeO}]_3$ . Table I also lists  $(n\text{-C}_4\text{H}_9)_2\text{GeCl}_2$ , previously mentioned without data.

Seven earlier publications establish the use of halides of certain transitional elements and elements in regular groups in the replacement of hydrogen attached to germanium in  $(\text{C}_2\text{H}_5)_3\text{GeH}$ ,<sup>2</sup>  $(n\text{-C}_4\text{H}_9)_2\text{GeH}_2$ <sup>3</sup> or  $n\text{-C}_4\text{H}_9\text{GeH}_3$ , to tin in  $(\text{C}_2\text{H}_5)_3\text{SnH}$  or to silicon in  $(\text{C}_2\text{H}_5)_3\text{SiH}$ <sup>4</sup> or  $(\text{C}_2\text{H}_5)_2\text{SiH}_2$ ,<sup>5</sup>  $n\text{-C}_7\text{H}_{15}\text{SiH}_3$ ,<sup>6</sup> cyclo- $\text{C}_6\text{H}_{11}\text{SiH}_3$ <sup>7</sup> or  $n\text{-C}_4\text{H}_9\text{SiH}_3$ .<sup>8</sup>

Partially substituted compounds such as  $n\text{-C}_7\text{H}_{15}\text{SiH}_2\text{Cl}$ ,<sup>6</sup>  $(\text{C}_2\text{H}_5)_2\text{SiHBr}$ ,<sup>5</sup> cyclo- $\text{C}_6\text{H}_{11}\text{SiH}_2\text{NCO}$ ,<sup>7</sup> cyclo- $\text{C}_6\text{H}_{11}\text{SiH}_2\text{NCS}$ <sup>7</sup> or  $n\text{-C}_4\text{H}_9\text{SiH}_2\text{I}$ <sup>8</sup> form easily in gradual addition of  $\text{HgCl}_2$ ,  $\text{HgBr}_2$ ,  $\text{AgNCO}$ ,  $\text{AgNCS}$  or  $\text{I}_2$  respectively to an excess of the appropriate alkylsilane or dialkylsilane. Similarly,  $n\text{-C}_4\text{H}_9\text{GeH}_2\text{Cl}$ ,  $n\text{-C}_4\text{H}_9\text{GeH}_2\text{Br}$ ,  $n\text{-C}_4\text{H}_9\text{GeH}_2\text{I}$ ,  $(n\text{-C}_4\text{H}_9)_2\text{GeHCl}$ ,  $(n\text{-C}_4\text{H}_9)_2\text{GeHBr}$  and  $(n\text{-C}_4\text{H}_9)_2\text{GeHI}$  form easily through gradual addition of  $\text{HgCl}_2$ ,  $\text{HgBr}_2$  or  $\text{I}_2$  to an excess of the appropriate *n*-butylgermane.<sup>3</sup>

This paper, in turn, demonstrates the reaction of  $(n\text{-C}_4\text{H}_9)_2\text{GeH}_2$  with a deficiency of either  $\text{Hg}(\text{SCN})_2$  or  $\text{Hg}(\text{CN})_2$  added gradually; the  $(n\text{-C}_4\text{H}_9)_2\text{GeHNCS}$  and  $(n\text{-C}_4\text{H}_9)_2\text{GeHCN}$  produced are apparently the first halogenoids of the  $\text{R}_2\text{GeHX}$  type in which R is an alkyl group and X is the halogenoid NCS or CN. Table I presents the properties and analyses of nine newly prepared compounds:  $(n\text{-C}_4\text{H}_9)_2\text{GeHNCS}$ ,  $(n\text{-C}_4\text{H}_9)_2\text{Ge}(\text{NCS})_2$ ,  $(n\text{-C}_4\text{H}_9)_2\text{GeHCN}$ ,  $(n\text{-C}_4\text{H}_9)_2\text{Ge}(\text{NCO})_2$ ,  $(n\text{-C}_4\text{H}_9)_2\text{Ge}[\text{N}(\text{CH}_3)_2]_2$ ,  $(n\text{-C}_4\text{H}_9)_2\text{GeF}_2$ ,  $(n\text{-C}_4\text{H}_9)_2\text{GeBr}_2$ ,  $(n\text{-C}_4\text{H}_9)_2\text{GeI}_2$  and  $[(n\text{-C}_4\text{H}_9)_2\text{GeO}]_3$ . Table I also presents adequate data for  $(n\text{-C}_4\text{H}_9)_2\text{GeCl}_2$ , previously mentioned without data.<sup>9</sup>

An unexpectedly favorable average yield of 74% for  $(n\text{-C}_4\text{H}_9)_2\text{GeHNCS}$  and  $(n\text{-C}_4\text{H}_9)_2\text{GeHCN}$  herein compares with an average yield of only 43% for cyclo- $\text{C}_6\text{H}_{11}\text{SiH}_2\text{NCO}$  and cyclo- $\text{C}_6\text{H}_{11}\text{SiH}_2\text{NCS}$ <sup>7</sup>; however,  $(n\text{-C}_4\text{H}_9)_2\text{GeHNCS}$  and  $\text{AgNCS}$  react at an extremely slow rate. Probably the unusually large molar volumes of tri-*n*-butylgermanium<sup>10</sup> and di-*n*-butylgermanium derivatives (approx-

mately 270 ml. for  $(n\text{-C}_4\text{H}_9)_2\text{GeHNCS}$  at the b.p.) offer some explanation.

The formulas  $\text{R}_2\text{GeHCN}$  and  $\text{R}_2\text{GeHNCS}$  are without proof of structure but follow earlier use of the structures  $(\text{CH}_3)_3\text{SiNCS}$ <sup>11,12</sup> and  $(\text{CH}_3)_3\text{SiCN}$ .<sup>13</sup>

## Experimental

**Starting Materials and Equipment.**—Approximately 36 g. of  $(n\text{-C}_4\text{H}_9)_2\text{GeH}_2$  and 4 g. each of  $(n\text{-C}_4\text{H}_9)_2\text{GeHCl}$ ,  $(n\text{-C}_4\text{H}_9)_2\text{GeHBr}$  and  $(n\text{-C}_4\text{H}_9)_2\text{GeHI}$  were available in sealed tubes after earlier investigations.<sup>3</sup> There was some subsequent conversion of surplus  $\text{R}_2\text{GeX}_2$  into carefully fractionally distilled  $(\text{R}_2\text{GeO})_3$ , which then served as a starting material. The customary equipment<sup>2-8</sup> included units with ground joints for preparations, also micro-pycnometers, micropipets for titrations and transfer pipets.

**Di-*n*-butylisothiocyanatogermane.**—Gradual addition (adding 1.75 g. every 20 minutes) over 1 hr. of 7.0 g. of  $\text{Hg}(\text{SCN})_2$  to 5.90 g. of  $(n\text{-C}_4\text{H}_9)_2\text{GeH}_2$  in an erlenmeyer flask and then heating on a hotplate to coagulate thiocyanuric acid furnished metallic mercury and a crude product with 19.1% NCS. Further addition of 1.5 g. of  $\text{Hg}(\text{SCN})_2$ , then coagulation of thiocyanuric acid by heating, next transfer and then washing the solid three times with small volumes of  $\text{CCl}_4$ , next extraction of the liquid three times with an equal volume of very hot water (the aqueous extracts were 0.4, 0.2 and finally 0.1 M in thiocyanic acid) and finally fractional distillation of the organogermanium layer furnished 5.95 g. (77% yield) of  $(n\text{-C}_4\text{H}_9)_2\text{GeHNCS}$ . Table I lists the center fraction, which contained both Ge-NCS and Ge-H, and which had an unmeasurable normal b.p. because of decomposition while the temperature rose gradually from 275 to 298°.

**Di-*n*-butyldiisothiocyanatogermane.**—Fifteen ml. of 2.5 M HNCS in diethyl ether and 4.06 g. of  $[(n\text{-C}_4\text{H}_9)_2\text{GeO}]_3$  soon formed 0.3 g. of water, later removed. The processing included heating to obtain insoluble thiocyanuric acid,<sup>14</sup> next filtering the thiocyanuric acid, then washing four times with  $\text{CCl}_4$  and finally fractional distillation to obtain 4.6 g. (76% yield) of  $(n\text{-C}_4\text{H}_9)_2\text{Ge}(\text{NCS})_2$ . Table I lists the center fraction.

**Di-*n*-butylcyanogermane.**—Ninety minutes reflux of 4.6 g. of  $(n\text{-C}_4\text{H}_9)_2\text{GeH}_2$  and 6.0 g. of  $\text{Hg}(\text{CN})_2$  (added every 20 minutes in 2 g. lots) produced hydrogen, hydrogen cyanide, metallic mercury and organogermanium compounds. Fractional distillation furnished 3.8 g. (72% yield) of crude  $(n\text{-C}_4\text{H}_9)_2\text{GeHCN}$ , b.p. 106–110° under 8 mm. pressure and 1.0 g. of higher boiling residue. Redistillation of the 3.8 g. gave 1.5 g. of center fraction compound listed in Table I. Both Ge-H and Ge-CN were present. Slow decomposition occurred at the normal b.p.

**Di-*n*-butyldiisocyanatogermane.**—Fifteen minutes free reflux, without solvent, of 9.30 g. of  $(n\text{-C}_4\text{H}_9)_2\text{GeI}_2$  and 14 g. of  $\text{AgNCO}$ , and then total distillation under 1 mm. pressure separated approximately 5.1 g. of volatile iodine-free liquid from  $\text{AgI}$  and  $\text{AgNCO}$  in the residue. Centrifuging

(1) Presented at 138th National Meeting, American Chemical Society, New York, N. Y., September, 1960.

(2) H. H. Anderson, *THIS JOURNAL*, **79**, 326 (1957).

(3) H. H. Anderson, *ibid.*, **82**, 3016 (1960).

(4) H. H. Anderson, *ibid.*, **79**, 4913 (1957).

(5) H. H. Anderson, *ibid.*, **80**, 5083 (1958).

(6) H. H. Anderson and A. Hendifar, *ibid.*, **81**, 1027 (1959).

(7) H. H. Anderson, *ibid.*, **81**, 4785 (1959).

(8) H. H. Anderson, *ibid.*, **82**, 1323 (1960).

(9) J. Satgé, R. Mathis-Noël and M. Lesbre, *Compt. rend.*, **249**, 131 (1959).

(10) H. H. Anderson, *THIS JOURNAL*, **73**, 5800 (1951).

(11) H. H. Anderson, *ibid.*, **69**, 3049 (1947); also references therein.

(12) J. Goubeau and J. Reykin, *Z. anorg. Chem.*, **294**, 96 (1958).

(13) R. Linton and E. R. Nixon, *J. Chem. Phys.*, **28**, 990 (1958).

(14) H. H. Anderson, *THIS JOURNAL*, **73**, 5439 (1951).

TABLE I  
 PROPERTIES OF NEW DI-*n*-BUTYLGERMANIUM COMPOUNDS (EXCEPT SEVENTH)

Compound	B.p., °C. <sup>d</sup>	<i>d</i> <sup>20</sup> <sub>4</sub>	<i>n</i> <sup>20</sup> <sub>c</sub>	—Molec. refr.—		Germanium <sup>a</sup>		Halogen(oid) <sup>b</sup>		Distilled at,	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	°C.	Mm.
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> GeHNCS	.. <sup>d</sup>	1.123	1.5097	65.63	65.46	29.5	29.2	23.6	23.7	96-98	1
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Ge(NCS) <sub>2</sub>	337	1.210	1.5501	80.04	79.78	23.9	23.6	38.4	38.5	140-141	1
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> GeHCN	243 <sup>d</sup>	1.050	1.4527	55.63	55.02	34.0	33.9	6.55 <sup>e</sup>	6.30	108-110	8
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Ge(NCO) <sub>2</sub>	273	1.179	1.4634	62.86	63.17	26.8	26.8	31.0	31.1	93-95	1
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Ge[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	249	1.001	1.4605	75.10	75.31	26.4	26.3	31.9	32.0	115-117	7
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> GeF <sub>2</sub> <sup>f</sup>	216	1.183	1.4222	48.14	48.20	32.3	..	16.9	17.2	102-103	14
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> GeCl <sub>2</sub> <sup>g</sup>	242	1.208	1.4724	59.24	59.79	28.2	27.7	27.5	27.8	107-108	8
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> GeBr <sub>2</sub>	269	1.565	1.5109	66.24	66.34	21.0	20.7	46.1	46.4	88-90	1
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> GeI <sub>2</sub>	304	1.863	1.5770	77.44	78.38	16.5	16.5	57.6	57.8	113-115	1
[( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> GeO] <sub>3</sub> <sup>h</sup>	359 <sup>d</sup>	1.161	1.4712	146.95 <sup>i</sup>	146.54	35.8	35.9	..	.. <sup>h</sup>	180-182	1

<sup>a</sup> Analyses for germanium involve use of fuming nitric and sulfuric acids, weighing GeO<sub>2</sub>. <sup>b</sup> Average of two closely agreeing determinations; determination of (CH<sub>3</sub>)<sub>2</sub>N- by Kjeldahl method. <sup>c</sup> In white light; all compounds are colorless. <sup>d</sup> With decomposition; decomposition of (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>GeHNCS was too rapid for determination of b.p. <sup>e</sup> Dumas nitrogen. <sup>f</sup> (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>GeF<sub>2</sub> melts at 10°. <sup>g</sup> Known compound, see ref. 9. <sup>h</sup> Trimeric oxide melts at -17°; calcd. for [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>GeO]<sub>3</sub>; mol. wt., 608.5; found: mol. wt., 570 (camphor). <sup>i</sup> See A. I. Vogel, W. T. Cresswell and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954). However, Ge-F taken as 2.05; Ge-Cl is questionable.

removed cyanuric acid; then redistillation separated 2.5 g. (67% yield) of crude (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Ge(NCO)<sub>2</sub>, b.p. 93-96° under 1 mm., from 2.2 g. of higher-boiling residue with only 16.1% NCO. Fractional distillation of the 2.5 g. furnished a 1.6 g. center cut listed in Table I.

**Di-*n*-butyl-bis-(dimethylamino)-germane.**—At 0°, 30 g. (an excess) of (CH<sub>3</sub>)<sub>2</sub>NH and 5.3 g. of (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>GeCl<sub>2</sub> in 14 ml. of *n*-hexane gave an instantaneous precipitate of (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>Cl. Storage for 1 hr. with occasional shaking, then the usual filtration and washing of (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>Cl and finally distillation<sup>15</sup> furnished 4.3 g. (79% yield) of (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>Ge[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>; fractional distillation produced a 1.75 g. center cut listed in Table I. The compound had a faint odor of amine and essentially no chlorine.

**Di-*n*-butyldifluorogermane.**—Heating 11.5 g. of (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>GeI<sub>2</sub> with 5.0 g., an excess, of resublimed SbF<sub>3</sub> furnished 5.9 g. (99% yield) of crude distilled (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>GeF<sub>2</sub>. Purification included centrifuging to remove a little SbI<sub>3</sub>, next addition of 0.2 g. of GeO<sub>2</sub> and then fractional distillation to obtain 2.7 g. of center cut (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>GeF<sub>2</sub>, b.p. 102.8-103.2° under 14 mm., listed in Table I.

**Di-*n*-butyldichlorogermane, Known.**—Heating of 5.25 g. of [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>GeO]<sub>3</sub> and 14.4 g. of 12 *M* HCl on a hotplate produced a mixture of immiscible liquids with vertical boundary layers. Addition of 10 g. of C<sub>2</sub>H<sub>5</sub>Br and then centrifuging and finally distillation furnished 6.52 g. (98% yield) of (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>GeCl<sub>2</sub>.

**Di-*n*-butyldibromogermane.**—Very careful addition of a slight excess of Br<sub>2</sub>-in-C<sub>2</sub>H<sub>5</sub>Br (50 vol. % each, with a continuous flow of 1 mg. of Br<sub>2</sub>/second) to 4.0 g. of gently swirled (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>GeH<sub>2</sub> in 5.6 g. of C<sub>2</sub>H<sub>5</sub>Br over 2 hr. replaced

Ge-H completely. Removal of the slight excess of bromine in an air stream followed; next, shaking with 1 g. of water (later removed) extracted extra HBr. Finally, distillation furnished 7.2 g. (99% yield) of (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>GeBr<sub>2</sub>; the center fraction had the properties in Table I.

**Di-*n*-butyldiiodogermane.**—Gradual addition of 17.4 g. (added in 6 lots of 2.9 g. each, one every 20 minutes), a slight excess, of powdered iodine to 6.4 g. of (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>GeH<sub>2</sub> with a little heat at the end changed all the Ge-H to Ge-I while HI gas escaped. Reflux with copper wire and then distillation under 1 mm. pressure furnished 15.3 g. (99% yield) of crude (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>GeI<sub>2</sub> containing 59.1% I. Shaking the crude compound twice for 5 minutes with 1.5 g. portions of water removed the extra HI from the organogermanium iodide. Then fractional distillation furnished a 4.3 g. center cut with the properties listed in Table I, also with very little odor.

**Di-*n*-butylgermanium Oxide Trimer.**—Shaking a combination of 4.8 g. of (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>GeF<sub>2</sub> and 4.8 g. of (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>GeBr<sub>2</sub> with 18 g. of warm 20% aqueous NaOH for 30 minutes produced an emulsion. A double extraction with 10 g. of CCl<sub>4</sub> each time, next centrifuging and then fractional distillation furnished 6.85 g. (94% yield) of [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>GeO]<sub>3</sub>; the 3.4 g. center cut had the properties listed in Table I. Determination of the b.p. under 760 mm. pressure caused the trimeric oxide to turn a light medium red rapidly.

**Other Reactions.**—One hr. reflux of 4.4 g. of (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>GeHNCS (analyzing 23.7% NCS) and 8 g. of AgNCS finally gave a product with only 24.8% NCS. This reaction proved surprisingly slow.

Reflux of 5 g. of (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>GeH<sub>2</sub> with 4 g. of AgNCO in 8 g. of CCl<sub>4</sub> for 1 hr. ultimately gave a center fraction containing much CN and some NCO; partial reduction of isocyanate to cyanide evidently occurred.

(15) H. H. Anderson, *THIS JOURNAL*, **74**, 1421 (1952).