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Di-*n*-butyldihalogermanes and Di-*n*-butylhalogenoidogermanes[1]

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Gradual addition of a deficiency of $Hg(CN)_2$ or $Hg(SCN)_2$ to previously known $(n\text{-}C_4H_9)_2GeH_2$ furnishes approximately 74% yields of $(n\text{-}C_4H_9)_2GeHCN$ or $(n\text{-}C_4H_9)_2GeHNCS$, respectively. These two latter compounds apparently are the first examples of the R_2GeHX type in which R is an alkyl group and X is the halogenoid CN or NCS. Very slow and gradual addition of bromine in C_2H_5Br to $(n\text{-}C_4H_9)_2GeH_2$ furnishes a high yield of $(n\text{-}C_4H_9)_2GeBr_2$. Successful preparation of $(n\text{-}C_4H_9)_2Ge(NCS)_2$ uses $[(n\text{-}C_4H_9)_2GeO]_3$ and HNCS in diethyl ether, rather than the extremely slow reaction of $(n\text{-}C_4H_9)_2GeHNCS$ and AgNCS. Table I lists the properties and analyses of nine newly prepared compounds: $(n\text{-}C_4H_9)_2GeHNCS$, $(n\text{-}C_4H_9)_2Ge(NCS)_2$, $(n\text{-}C_4H_9)_2GeHCN$, $(n\text{-}C_4H_9)_2Ge(NCO)_2$, $(n\text{-}C_4H_9)_2Ge[N(CH_3)_2]_2$, $(n\text{-}C_4H_9)_2GeF_2$, $(n\text{-}C_4H_9)_2GeBr_2$, $(n\text{-}C_4H_9)_2GeI_2$ and $[(n\text{-}C_4H_9)_2GeO]_3$. Table I also lists $(n\text{-}C_4H_9)_2GeCl_2$, 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 $(C_2H_5)_3GeH$,[2] $(n\text{-}C_4H_9)_2GeH_2$[3] or $n\text{-}C_4H_9GeH_3$, to tin in $(C_2H_5)_3SnH$ or to silicon in $(C_2H_5)_3SiH$[4] or $(C_2H_5)_2SiH_2$,[5] $n\text{-}C_7H_{15}SiH_3$,[6] cyclo-$C_6H_{11}SiH_3$[7] or $n\text{-}C_4H_9SiH_3$.[8]

Partially substituted compounds such as $n\text{-}C_7H_{15}SiH_2Cl$,[6] $(C_2H_5)_2SiHBr$,[5] cyclo-$C_6H_{11}SiH_2NCO$,[7] cyclo-$C_6H_{11}SiH_2NCS$[7] or $n\text{-}C_4H_9SiH_2I$[8] form easily in gradual addition of $HgCl_2$, $HgBr_2$, AgNCO, AgNCS or I_2 respectively to an excess of the appropriate alkylsilane or dialkylsilane. Similarly, $n\text{-}C_4H_9GeH_2Cl$, $n\text{-}C_4H_9GeH_2Br$, $n\text{-}C_4H_9GeH_2I$, $(n\text{-}C_4H_9)_2GeHCl$, $(n\text{-}C_4H_9)_2GeHBr$ and $(n\text{-}C_4H_9)_2GeHI$ form easily through gradual addition of $HgCl_2$, $HgBr_2$ or I_2 to an excess of the appropriate n-butylgermane.[3]

This paper, in turn, demonstrates the reaction of $(n\text{-}C_4H_9)_2GeH_2$ with a deficiency of either $Hg(SCN)_2$ or $Hg(CN)_2$ added gradually; the $(n\text{-}C_4H_9)_2GeHNCS$ and $(n\text{-}C_4H_9)_2GeHCN$ produced are apparently the first halogenoids of the R_2GeHX 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: $(n\text{-}C_4H_9)_2GeHNCS$, $(n\text{-}C_4H_9)_2Ge(NCS)_2$, $(n\text{-}C_4H_9)_2GeHCN$. $(n\text{-}C_4H_9)_2Ge(NCO)_2$, $(n\text{-}C_4H_9)_2Ge[N(CH_3)_2]_2$, $(n\text{-}C_4H_9)_2GeF_2$, $(n\text{-}C_4H_9)_2GeBr_2$, $(n\text{-}C_4H_9)_2GeI_2$ and $[(n\text{-}C_4H_9)_2GeO]_3$. Table I also presents adequate data for $(n\text{-}C_4H_9)_2GeCl_2$, previously mentioned without data.[9]

An unexpectedly favorable average yield of 74% for $(n\text{-}C_4H_9)_2GeHNCS$ and $(n\text{-}C_4H_9)_2GeHCN$ herein compares with an average yield of only 43% for cyclo-$C_6H_{11}SiH_2NCO$ and cyclo-$C_6H_{11}SiH_2NCS$[7]; however, $(n\text{-}C_4H_9)_2GeHNCS$ and AgNCS react at an extremely slow rate. Probably the unusually large molar volumes of tri-n-butylgermanium[10] and di-n-butylgermanium derivatives (approximately 270 ml. for $(n\text{-}C_4H_9)_2GeHNCS$ at the b.p.) offer some explanation.

The formulas R_2GeHCN and $R_2GeHNCS$ are without proof of structure but follow earlier use of the structures $(CH_3)_3SiNCS$[11,12] and $(CH_3)_3SiCN$.[13]

Experimental

Starting Materials and Equipment.—Approximately 36 g. of $(n\text{-}C_4H_9)_2GeH_2$ and 4 g. each of $(n\text{-}C_4H_9)_2GeHCl$, $(n\text{-}C_4H_9)_2GeHBr$ and $(n\text{-}C_4H_9)_2GeHI$ were available in sealed tubes after earlier investigations.[3] There was some subsequent conversion of surplus R_2GeX_2 into carefully fractionally distilled $(R_2GeO)_3$, which then served as a starting material. The customary equipment[2-8] 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 $Hg(SCN)_2$ to 5.90 g. of $(n\text{-}C_4H_9)_2GeH_2$ 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 $Hg(SCN)_2$, then coagulation of thiocyanuric acid by heating, next transfer and then washing the solid three times with small volumes of 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 $(n\text{-}C_4H_9)_2GeHNCS$. 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 $[(n\text{-}C_4H_9)_2GeO]_3$ soon formed 0.3 g. of water, later removed. The processing included heating to obtain insoluble thiocyanuric acid,[14] next filtering the thiocyanuric acid, then washing four times with CCl_4 and finally fractional distillation to obtain 4.6 g. (76% yield) of $(n\text{-}C_4H_9)_2Ge(NCS)_2$. Table I lists the center fraction.

Di-*n*-butylcyanogermane.—Ninety minutes reflux of 4.6 g. of $(n\text{-}C_4H_9)_2GeH_2$ and 6.0 g. of $Hg(CN)_2$ (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 $(n\text{-}C_4H_9)_2GeHCN$, 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 $(n\text{-}C_4H_9)_2GeI_2$ and 14 g. of AgNCO, and then total distillation under 1 mm. pressure separated approximately 5.1 g. of volatile iodine-free liquid from AgI and AgNCO in the residue. Centrifuging

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(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.	d^{20}_4	n^{20}[c]	Molec. refr.		Germanium[a]		Halogen(oid)[b]		Distilled at,	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	°C.	Mm.
$(n\text{-}C_4H_9)_2GeHNCS$	..[d]	1.123	1.5097	65.63	65.46	29.5	29.2	23.6	23.7	96–98	1
$(n\text{-}C_4H_9)_2Ge(NCS)_2$	337	1.210	1.5501	80.04	79.78	23.9	23.6	38.4	38.5	140–141	1
$(n\text{-}C_4H_9)_2GeHCN$	243[d]	1.050	1.4527	55.63	55.02	34.0	33.9	6.55[e]	6.30	108–110	8
$(n\text{-}C_4H_9)_2Ge(NCO)_2$	273	1.179	1.4634	62.86	63.17	26.8	26.8	31.0	31.1	93–95	1
$(n\text{-}C_4H_9)_2Ge[N(CH_3)_2]_2$	249	1.001	1.4605	75.10	75.31	26.4	26.3	31.9	32.0	115–117	7
$(n\text{-}C_4H_9)_2GeF_2$[f]	216	1.183	1.4222	48.14	48.20	32.3	..	16.9	17.2	102–103	14
$(n\text{-}C_4H_9)_2GeCl_2$[g]	242	1.208	1.4724	59.24	59.79	28.2	27.7	27.5	27.8	107–108	8
$(n\text{-}C_4H_9)_2GeBr_2$	269	1.565	1.5109	66.24	66.34	21.0	20.7	46.1	46.4	88–90	1
$(n\text{-}C_4H_9)_2GeI_2$	304	1.863	1.5770	77.44	78.38	16.5	16.5	57.6	57.8	113–115	1
$[(n\text{-}C_4H_9)_2GeO]_3$[h]	359[d]	1.161	1.4712	146.95[i]	146.54	35.8	35.9	..	..[h]	180–182	1

[a] Analyses for germanium involve use of fuming nitric and sulfuric acids, weighing GeO_2. [b] Average of two closely agreeing determinations; determination of $(CH_3)_2N-$ by Kjeldahl method. [c] In white light; all compounds are colorless. [d] With decomposition; decomposition of $(n\text{-}C_4H_9)_2GeHNCS$ was too rapid for determination of b.p. [e] Dumas nitrogen. [f] $(n\text{-}C_4H_9)_2GeF_2$ melts at 10°. [g] Known compound, see ref. 9. [h] Trimeric oxide melts at −17°; calcd. for $[(n\text{-}C_4H_9)_2GeO]_3$: mol. wt., 608.5; found: mol. wt., 570 (camphor). [i] 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 $(n\text{-}C_4H_9)_2Ge(NCO)_2$, 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 $(CH_3)_2NH$ and 5.3 g. of $(n\text{-}C_4H_9)_2GeCl_2$ in 14 ml. of *n*-hexane gave an instantaneous precipitate of $(CH_3)_2NH_2Cl$. Storage for 1 hr. with occasional shaking, then the usual filtration and washing of $(CH_3)_2NH_2Cl$ and finally distillation[15] furnished 4.3 g. (79% yield) of $(n\text{-}C_4H_9)_2Ge[N(CH_3)_2]_2$; 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 $(n\text{-}C_4H_9)_2GeI_2$ with 5.0 g., an excess, of resublimed SbF_3 furnished 5.9 g. (99% yield) of crude distilled $(n\text{-}C_4H_9)_2GeF_2$. Purification included centrifuging to remove a little SbI_3, next addition of 0.2 g. of GeO_2 and then fractional distillation to obtain 2.7 g. of center cut $(n\text{-}C_4H_9)_2GeF_2$, b.p. 102.8–103.2° under 14 mm., listed in Table I.

Di-*n*-butyldichlorogermane, Known.—Heating of 5.25 g. of $[(n\text{-}C_4H_9)_2GeO]_3$ 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_2H_5Br and then centrifuging and finally distillation furnished 6.52 g. (98% yield) of $(n\text{-}C_4H_9)_2GeCl_2$.

Di-*n*-butyldibromogermane.—Very careful addition of a slight excess of Br_2-in-C_2H_5Br (50 vol. % each, with a continuous flow of 1 mg. of Br_2/second) to 4.0 g. of gently swirled $(n\text{-}C_4H_9)_2GeH_2$ in 5.6 g. of C_2H_5Br 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 $(n\text{-}C_4H_9)_2GeBr_2$; 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 $(n\text{-}C_4H_9)_2GeH_2$ 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 $(n\text{-}C_4H_9)_2GeI_2$ 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 $(n\text{-}C_4H_9)_2GeF_2$ and 4.8 g. of $(n\text{-}C_4H_9)_2GeBr_2$ with 18 g. of warm 20% aqueous NaOH for 30 minutes produced an emulsion. A double extraction with 10 g. of CCl_4 each time, next centrifuging and then fractional distillation furnished 6.85 g. (94% yield) of $[(n\text{-}C_4H_9)_2GeO]_3$; 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 $(n\text{-}C_4H_9)_2GeHNCS$ (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 $(n\text{-}C_4H_9)_2GeH_2$ with 4 g. of AgNCO in 8 g. of CCl_4 for 1 hr. ultimately gave a center fraction containing much CN and some NCO; partial reduction of isocyanate to cyanide evidently occurred.

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