[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Tri-n-butylgermanium Esters, Halides, Isocyanate and Oxide

BY HERBERT H. ANDERSON

A four-hour reflux of n-Bu_4Ge and iodine yields n-Bu_3GeI, which upon alkaline hydrolysis furnishes $(n\text{-}Bu_3Ge)_2O$; this oxide reacts with acids producing halides or esters. Table I lists the properties of n-Bu_4Ge and the new compounds: $(n\text{-}Bu_3Ge)_2O$, n-Bu_3GeF, n-Bu_3GeCl, n-Bu_3GeBr, n-Bu_3GeI, n-$Bu_3Ge(NCO)$, n-$Bu_3Ge(HCOO)$, n-$Bu_3Ge(CH_3COO)$, n-$Bu_3Ge(CF_3COO)$ and n-$Bu_3Ge(n\text{-}C_6H_{13}COO)$. Associated with the unusually large molar volumes of these liquid germanium compounds—320 ml. for n-Bu_3GeF, the smallest—a pattern of four tendencies persists, namely: to have no melting point, being vitreous at low temperatures; to retain small amounts of free acids despite reflux at low pressure; to react slowly, as compared with Et_3GeX or n-Pr_3GeX analogs; to be relatively insoluble in water. New preparative methods include the combinations n-$Bu_4Ge + I_2$, n-$Bu_3Ge(CH_3COO) + n\text{-}C_6H_{13}COOH$, n-$Bu_3GeI + Ag(CH_3COO)$.

This investigation extends the scope of known tri-n-alkylgermanium derivatives through presentation of the butyl members, which have some properties indicative of large molecules, but which do not offer steric hindrance. In keeping with difficulties encountered, new or modified methods are introduced.

It is interesting and enlightening to consider trialkylgermanium compounds in terms of molar volumes, which are as follows for the R_3Ge group, in ml. (at the boiling point): Me_3Ge, 112; Et_3Ge, 175; n-Pr_3Ge, 250; n-Bu_3Ge, 310; n-Am_3Ge, yet unknown, 370, estimated. For $(n\text{-}Bu_3Ge)_2O$ the volume is approximately 650 ml., while the largest ester, n-$Bu_3Ge(n\text{-}C_6H_{13}COO)$, has a volume of approximately 500 ml., and the smallest halide, n-Bu_3GeF, has a volume of 320 ml. These volumes depend on estimated densities at the boiling points and are not exact, but are perhaps within 5% of the true value on the average. The organic free radical triphenylmethyl has an estimated molar volume of approximately 300 ml., calculated as a liquid, and is smaller than all the tri-n-butylgermanium compounds.

All ten new tri-n-butylgermanium derivatives are truly large molecules, and thus it is no surprise that the actual properties are somewhat different from those of the corresponding trimethylgermanium or triethylgermanium halides, esters and oxides. In fact, if one extrapolates to tri-n-amyl or to tri-n-hexyl analogs, then it should be quite difficult to obtain pure compounds unless recrystallization becomes possible. Fortunately the relatively compact tricyclohexylgermanium halides are solids with melting points in the vicinity of 100°, and can be crystallized from solution.[1,2]

Actual observations indicating large molecules included the following: eight compounds became vitreous at low temperatures, while only $(n\text{-}Bu_3Ge)_2O$, n-Bu_3GeF and n-$Bu_3Ge(NCO)$ had melting points; despite reflux at low pressure, small amounts of free acid were retained throughout, more so than with the corresponding tri-n-propylgermanium halides or esters[3]; instances of unexpectedly slow reaction rates were the persistence of 20% of unchanged oxide in the heating of HCOOH and $(n\text{-}Pr_3Ge)_2O$, also the persistence of 20% of n-Bu_3GeBr in the reaction of excess n-BuMgBr with $GeBr_4$, likewise the slow reaction of the organogermanium oxide with 48% HF or with excess HCl; a relatively low solubility of the organogermanium derivatives in water and also of water in the organogermanium compounds proved advantageous in the handling of the new compounds. Of course the high boiling points of all the compounds are also substantiation for large size.

At reflux temperature iodine reacts with n-Bu_4Ge to give n-Bu_3GeI, but iodine does not react with n-Pr_4Ge at the reflux temperature; yet in a sealed tube at approximately 200° the story may include displacement of a propyl group.

Such an iodination is novel for alkylgermanium procedures, as are the transesterification of n-$Bu_3Ge(CH_3COO)$ with heptanoic acid and also the reaction of n-Bu_3GeI with $Ag(CH_3COO)$; boiling of $(n\text{-}Bu_3Ge)_2O$ and concentrated HCl together ensured complete reaction, which might have been quite slow at room temperature.

Table I lists the properties of the ten new compounds and also of n-Bu_4Ge, which Orndorff, Tabern and Dennis undoubtedly prepared, but for which they present a boiling point of 178–180° at 733 mm. as the only definite property[4]; such a boiling point is obviously impossible and represents either a typographical error or an error of some other kind. Their analyses indicate successful isolation of n-Bu_4Ge. A boiling point of 278° as reported herein, is reasonable, since n-Pr_4Ge boils at 226°.

Experimental

Tetra-n-butylgermanium.—Fifty-three grams of pure $GeBr_4$ and 600 ml. of 1.3 M n-C_4H_9MgBr (an excess of 45%) in diethyl ether reacted easily, but formed two layers during a half-hour reflux on a steam-bath, so the mixture was shaken persistently. After gradual aqueous decomposition of the excess n-BuMgBr, the organogermanium layer was separated, then shaken with excess 30% NaOH solution to convert n-Bu_3GeBr into $(n\text{-}Bu_3Ge)_2O$. Next came filtration, use of some (30–60°) petroleum ether to complete recovery from the aqueous solution, then drying with Na_2SO_4 overnight. Distillation of the solvent left 36 g. of product; further distillation, under 17 mm. pressure, yielded a center fraction of n-Bu_4Ge at 160–161° and also a residue of 6.5 g. boiling above 218°, undoubtedly $(n\text{-}Bu_3Ge)_2O$. Thus only 74% of the germanium went to n-Bu_4Ge, while 20% remained as n-Bu_3GeBr, later converted to oxide for easy separation. Reflux in a solvent boiling at approximately 100° might be better in this Grignard reaction. Table I lists the correct boiling point of 278° for n-Bu_4Ge.

Preparation of New Compounds.—Because of previous descriptions of the methods, most of the minor details are omitted when feasible.

Bis-(tri-n-butylgermanium) Oxide.—Using equipment with ground joints, 25.5 g. of pure n-Bu_4Ge and an initial

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(1) H. Bauer and K. Burschkies, *Ber.*, **65**, 956 (1932).

(2) O. H. Johnson and W. H. Nebergall, THIS JOURNAL, **71**, 1720 (1949).

(3) H. H. Anderson, *ibid.*, **73**, 5440 (1951).

(4) (a) W. R. Orndorff, D. L. Tabern and L. M. Dennis, *ibid.*, **49**, 2512 (1927); (b) H. Gilman and R. W. Leeper, *J. Org. Chem.*, **16**, 466 (1951), give a boiling point of 127–128° at 4 mm.

TABLE I

All distillations at low pressure. Measured density of the trifluoroacetate, 1.148, later corrected for free acid. M.p.'s of oxide, fluoride and isocyanate were −42, −12 and −47°, respectively.

Compound	B.p., °C.	Mm.	d^{20}_4	n^{20}	R, ml.	Mol. wt.		RCOO or halogen	
						Calcd.	Found	Calcd.	Found
n-Bu$_4$Ge	278	760	0.934	1.4571	87.8	...	...	..	
	160–161	17							
(*n*-Bu$_3$Ge)$_2$O	353	760	1.027	1.4652	135.7	503.9	518	28.9	28.5 (Ge)
	173–174	1							
n-Bu$_3$GeF	245	760	1.038	1.4419	67.0	262.9	258	7.2	7.9, 7.9
	128–130	14							
n-Bu$_3$GeCl	271	760	1.054	1.4652	73.3	279.4	284	12.7	12.9, 12.9
	139–140	13							
n-Bu$_3$GeBr	279	760	1.195	1.4809	77.1	323.9	324	24.7	24.8, 24.7
	143–144	10							
n-Bu$_3$GeI[a]	297	760	1.340	1.508	82.6	370.9	358	34.2	34.7, 34.8
	163–164	15							
n-Bu$_3$Ge(HCOO)	267	760	1.051	1.4538	74.4	289.0	285	15.6	16.1, 16.2
	149–151	16							
n-Bu$_3$Ge(CH$_3$COO)	272	760	1.027	1.4514	79.3	303.0	312	19.5	19.6, 19.7
	147–148	14							
n-Bu$_3$Ge(CF$_3$COO)	262	760	1.144	1.419	...	357.0	370	31.6	32.6, 32.6
	147–149	19							
n-Bu$_3$Ge(*n*-C$_6$H$_{13}$COO)	324 dec.	760	0.988	1.4539	102.2	373.1	353	34.6	35.3, 35.2
	147–148	1							
n-Bu$_3$Ge(NCO)	283	760	1.044	1.4595	75.0	286.0	280	14.7	14.9, 14.8
	109–110	2							

[a] Ref. 4b records b.p. 125–127° at 4 mm., but report no properties of the oxide.

5 g. of iodine were heated together with reflux of first iodine and later *n*-BuI until most of the iodine reacted; then three 5-g. lots of iodine and a final 2-g. lot were added, this requiring two hours; after two more hours of reflux (total heating, four hours), very little free iodine remained. Thereupon, distillation separated 13.9 g. of *n*-BuI and left 33 g. of crude *n*-Bu$_3$GeI; the reaction was nearly quantitative. After hydrolysis of *n*-Bu$_3$GeI with excess 15% aqueous NaOH, the layers were separated, the organogermanium layer filtered to remove a small amount of carbon, some (30–60°) petroleum ether used for quantitative recovery of the (*n*-Bu$_3$Ge)$_2$O; then the solution dried over Na$_2$SO$_4$ overnight. Following distillation of the solvent, hardly 0.1 g. of unchanged *n*-Bu$_4$Ge remained; a center fraction of (*n*-Bu$_3$Ge)$_2$O boiled at 173–174° under 1 mm. pressure. Table I lists the properties of the oxide—a clear, colorless liquid which is a bit more viscous than is CCl$_4$; total yield of oxide, 20 g.

Halides and Isocyanate.—Although heated to boiling, excess 60% aqueous KHF$_2$ converted (*n*-Bu$_3$Ge)$_2$O only 50% into *n*-Bu$_3$GeF. Using a transparent plastic test-tube, 5 g. of oxide and 15 g. of 48% HF when stirred for 25 minutes furnished an 80% yield of *n*-Bu$_3$GeF, while at least a gram of unchanged oxide remained; after the usual extraction with light petroleum ether, then drying and distillation of solvent, a center fraction of fluoride was collected as in Table I.

Six grams of oxide and 12 ml. of 12 *M* HCl were brought to a boil, shaken, and extracted with light petroleum ether, yielding a product containing 14.0% Cl, or 1.3% free HCl. Boiling with 0.4 g. of fresh oxide for several minutes at 760 mm. yielded a center fraction with 13.3% Cl; again boiling with another 0.4 g. of oxide furnished a center cut with 12.9% Cl, or 0.2% free HCl. Thus the oxide reacts slowly with small amounts of acid.

Five grams of oxide and 12 ml. of 48% HBr were heated to boiling, let stand a half-hour, and then the organogermanium layer was separated mechanically, then boiled, cooled and finally boiled for two minutes with 0.15 g. of NaOH in small pieces. As with the chloride and the iodide, the yield was essentially quantitative. Table I lists the properties of the center cut.

Similarly, 8 g. of oxide and 31 g. of concentrated HI solution yielded a first product with 37.0% I and a product after treatment with NaOH the center fraction of which contained 34.7% I, with the properties of Table I.

Seven grams of pure *n*-Bu$_3$GeCl and 12 g. of AgNCO reacted in boiling benzene in the typical isocyanate process, using 25 ml. of benzene and 2 ml. of nitromethane, however, to furnish *n*-Bu$_3$Ge(NCO) essentially quantitatively.[5]

Esters.—Twenty minutes of free reflux with 3 ml. of 90% formic acid and 4.4 g. of oxide were inadequate; distillation of the acid, then reflux with two ml. of fresh acid still left at least one ml. of unchanged oxide. Yet the center fraction of the ester contained 0.5% free acid. Incomplete reaction and incomplete separation indicate difficulties with "large molecules" not encountered with Et$_3$Ge(HCOO).[6]

In contrast, the silver salt turned yellow instantly when 11 g. of Ag(CH$_3$COO) was added to 7 g. of *n*-Bu$_3$GeI in 30 ml. of benzene, followed by a half-hour of reflux, and the center fraction of the 5.6 g. product contained only 0.2% of free acetic acid; obviously such a process which avoids large amounts of acid or acid anhydride is highly advantageous. This method has not been demonstrated for trialkylgermanium esters before.

Upon ten minutes of free reflux 5 g. of *n*-Bu$_3$Ge(CH$_3$COO) and 3.6 g. of *n*-heptanoic acid liberated 0.95 g. of crude acetic acid, which distilled out of the system; the center cut of *n*-Bu$_3$Ge(C$_6$H$_{13}$COO), taken at one mm., contained 0.6% of free heptanoic acid, but no effort was made to remove this small amount of free acid, because of limited stabilities. This is a transesterification.

Four grams of pure oxide and 4 g. of CF$_3$COOH reacted with much warming to give an opalescence; after cautious heating, the main body of water was separated by centrifuging; the yield was quantitative. Because 33.1% CF$_3$COO was present in the center fraction, the ester was refluxed with 0.3 g. of fresh oxide, whereupon 1.0% of free CF$_3$COOH remained in the center cut listed in Table I.

Properties, Analysis and Equipment.—Only the oxide, fluoride and isocyanate have melting points, all the others being viscous at low temperature. All are colorless liquids; the oxide is somewhat more viscous than is CCl$_4$, while the others are fairly mobile. The fluoride has a faint sweet odor, while the other compounds have very little odor. In all probability the data in Table I are quite close except for the densities of the iodide and trifluoroacetate which are about 4 parts per thousand in question. Experimental difficulties set a limit to accuracy, since it is not simple to prepare extremely pure compounds. Good pycnometers and micropipets served for densities and analyses, respec-

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[5] G. S. Forbes and H. H. Anderson, THIS JOURNAL, **62**, 761 (1940); H. H. Anderson, *ibid.*, **71**, 1799 (1949); **72**, 196 (1950).

[6] H. H. Anderson, *ibid.*, **72**, 2089 (1950).

tively. Analyses consisted of titration of the available acidity and of molecular weights by depressing the freezing point of camphor; fuming nitric acid and sulfuric acid converted the organogermanium oxide finally into GeO_2. Refractive indices are in white light.

Interchangeable equipment was used, bearing ground joints and thermometers with ground joints; all transfers were by pipet.

CAMBRIDGE 38, MASS. RECEIVED JULY 13, 1951

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Methylanilinosilanes and Ethylanilinosilanes; Reactions of Anilinosilanes

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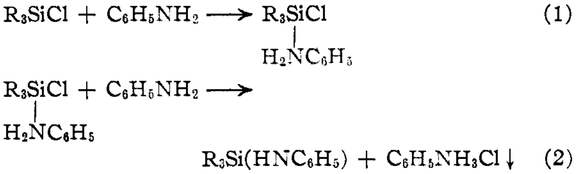
Methylchlorosilanes, ethylchlorosilanes and diphenyldichlorosilane react with aniline to furnish anilinium chloride and five (new) methylanilinosilanes, ethylanilinosilanes and diphenyldianilinosilane, the properties of which are in Table I. Alkylanilinosilanes react with various acids, especially inorganic acids. Trimethylchlorosilane and triethylchlorosilane react reversibly with aniline $R_3SiCl + 2C_6H_5NH_2 \leftrightarrows R_3Si(HNC_6H_5) + C_6H_5NH_3Cl$. A study of numerous exchange reactions, such as $4(CH_3)_3Si(HNC_6H_5) + SiBr_4 \rightarrow 4(CH_3)_3SiBr + Si(HNC_6H_5)_4$, indicates that substituted alkylsilanes react easily under reflux conditions, accompanied by the distillation of the most volatile component possible; alkyl groups do not migrate.

Ruff[1] converted trichlorosilane into triiodosilane, in benzene solution, and recently we similarly prepared numerous new alkyliodosilanes by the same method[2,3]; the following equations illustrate the principles involved (for Ruff R was hydrogen)

$$RSiCl_3 + 6C_6H_5NH_2 \longrightarrow RSi(HNC_6H_5)_3 + 3C_6H_5NH_3Cl\downarrow$$

$$RSi(HNC_6H_5)_3 + 6HI \longrightarrow RSiI_3 + 3C_6H_5NH_3I\downarrow$$

As done in the manner recommended by Ruff,[1] dialkyldiiodosilanes could be prepared, but trialkyliodosilanes could not be made.[2] The following equations represent the first step of the Ruff process for R_3SiX



$$R_3SiCl + C_6H_5NH_2 \longrightarrow \underset{\displaystyle H_2NC_6H_5}{\underset{|}{R_3SiCl}} \qquad (1)$$

$$\underset{\displaystyle H_2NC_6H_5}{\underset{|}{R_3SiCl}} + C_6H_5NH_2 \longrightarrow R_3Si(HNC_6H_5) + C_6H_5NH_3Cl\downarrow \qquad (2)$$

This process is rapid when conditions are forcing, namely: omission of solvent benzene; reaction at 25° or lower. On the other hand, high temperature results in a reversal, with formation of a completely liquid system, and solvent also prevents reaction, at least the step in the second equation. In the first equation the silane with five substituents decomposes with elimination of HCl, which combines with a molecule of aniline in the second equation to produce insoluble anilinium chloride.

By using the forcing conditions to convert $(CH_3)_3SiCl$ into the anilino derivative, and then dissolving the anilino compound in benzene, followed by use of pure HI gas, it should be possible to prepare $(CH_3)_3SiI$.

Table II presents a number of exchange reactions; these constitute a new approach to preparative problems. At present there is a "volatility series" $(C_6H_5NH)\rightarrow(C_2H_5)_2N\rightarrow I\rightarrow Br\rightarrow Cl\rightarrow F$, with slight uncertainty regarding the diethylamino group and iodine; the element or group as far to the right in this series as possible appears in the most volatile compound, which distils out of the system. Alkylamino derivatives of silanes enter exchange reactions easily with halides of silicon, phosphorus and germanium, as well as aniline or anilinium halides. This "volatility series" appears to be associated with volumes of groups or atoms, rather than with masses (weights).

Larsson and Mjörne have already prepared trimethylanilinosilane,[4a] listed as b.p. 96–98° under 24 mm., from $(Me_3Si)_2NH$ and aniline, also triethylanilinosilane,[4b] listed as b.p. 130–132° under 12 mm., from triethylchlorosilane and aniline. There are some advantages in making the trimethylanilinosilane from the chloro compound, the process being shorter and perhaps more exact.

Experimental

Preparation of Alkylanilinosilanes and Diphenyldianilinosilane (a) Alkyltrianilinosilanes and Dialkyldianilinosilanes.—Because the preparations of the monomethyl, monoethyl and diethyl derivatives are similar, only directions for making the dimethyl analog are necessary. Twenty grams of dimethyldichlorosilane and 70 g. of aniline (2.4 mols. of aniline per chlorine atom) upon combination in 150 ml. of pure benzene reacted with much heat; after a half-hour of reflux, with shaking, the mixture cooled overnight; then the precipitate of anilinium chloride was filtered, washed with benzene and discarded. The filtrate contained benzene, excess aniline and dimethyldianilinosilane; after distilling the benzene and nearly all the aniline—up to 250° at 760 mm.—the remaining liquid was transferred to smaller distillation equipment and finally a center fraction taken at low pressure as in Table I. A single unit of Pyrex glass, except for a thermometer with a ground joint, was the best equipment for monoalkyl derivatives, while dialkyl derivatives could tolerate a receiver with a ground joint. According to volumes involved, yields were about 80%.

(b) **Trialkylanilinosilanes.**—Thirty grams of pure Et_3SiCl and 45 g. of aniline (7 g. excess) formed much precipitate in the cold, but the precipitate redissolved when heated to 140° and then the solution boiled at 158°; after standing at 0° overnight, the pasty mass was filtered using suction and pressing as dry as possible, but without washing; the solid discarded. Careful distillation of the 37 g. of filtrate furnished 7 g. of excess aniline and then, as in Table I, 30 g. of triethylanilinosilane, or a yield of 72%.

Forty-eight grams of $(CH_3)_3SiCl$ and 26 g. of aniline, a deficiency, reacted with a temperature rise of 38°; after cooling to 0°, the pasty mass was filtered without washing, on a buchner funnel. Then distillation yielded first unchanged trimethylchlorosilane and later 13 g., or 56% based on aniline, of trimethylanilinosilane. A center cut was collected as in Table I.

(c) **Diphenyldianilinosilane.**—Twenty grams of diphenyldichlorosilane and 50 g. of aniline in 40 ml. of benzene fur-

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(1) O. Ruff, *Ber.*, **41**, 3738 (1908).

(2) H. H. Anderson, D. L. Seaton and R. P. T. Rudnicki, THIS JOURNAL, **73**, 2144 (1951).

(3) H. H. Anderson, *ibid.*, **73**, 2351 (151).

(4) (a) E. Larsson and O. Mjörne, *Kem. Tid.* (*Sweden*), **61**, 59 (1949). (b) O. Mjörne, *ibid.*, **62**, 120 (1950); see *Chem. Abstr.*, **43**, 5739*d* (1949); **44**, 1402*f*, 9342*f* (1950).