[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Tri-*n*-propylgermanium Esters and Sulfate; Transesterifications

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Bis-(tri-*n*-propylgermanium) oxide reacts with the appropriate organic acid to yield the following seven (new) tri-*n*-propylgermanium esters: formate, acetate, propionate, trifluoroacetate, monochloroacetate, dichloroacetate, also monobromoacetate. Distillation under diminished pressure is needed with the monochloroacetate, dichloroacetate and monobromoacetate, while the trichloroacetate is unstable. Seven transesterifications are reported, including the (new) compound bis-(tri-*n*-propylgermanium) sulfate, as prepared from tri-*n*-propylgermanium propionate and 100% sulfuric acid. In a transesterification the less volatile acid displaces the more volatile acid from an ester.

A previous paper made feasible an investigation of organogermanium esters using the previous methods,[1] which consisted of the reaction of a trialkylgermanium oxide—or a dialkylgermanium oxide—with either an organic acid or an anhydride of an organic acid. This present paper now includes derivatives of halogeno-organic acids, thus widening the scope.

As far as is known, the transesterification method is new for organogermanium compounds. Under the experimental conditions, the equilibrium $R_3GeOCOR' + HOCOR'' \rightleftarrows R_3GeOCOR'' + HOCOR'$ is easily upset by distilling out the more volatile acid using equipment of five theoretical plates and a period of 15 minutes or less. Conceivably the actual mechanism may not be so simple, and one should remember that the oxide $(R_3Ge)_2O$ could be involved. In support of the transesterification method, there are now seven reactions, which the individual reader may consider as transesterifications, displacements or ester exchanges. Sulfuric acid is a dibasic acid which displaces more volatile acids. In no single instance did a less volatile acid fail to liberate a more volatile acid from an ester.

In the decomposition of tri-*n*-propylgermanium monochloroacetate and other chloroacetates and the monobromoacetate, the nature of the process is still uncertain, although it is quite definite that the decomposition is accompanied by formation of hydrolyzable chloride, also extra available acidity. No claim of proof of decomposition products is offered; it seems that propyl groups are too large for satisfactory identification of any compounds produced in a decomposition. By extension of known trends in Group IV, it appears likely that a compound such as $Et_3Sn(OCOCH_2Cl)$ would not be too stable; $Me_3Si(OCOCH_2Cl)$, now known, and being reported elsewhere, is a fairly stable compound.

Preparation of New Esters.—Bis-(tri-*n*-propylgermanium) oxide, described in a separate paper, is the product of a reaction between tetra-*n*-propylgermanium and bromine, followed by hydrolysis with aqueous alkali; the oxide is a liquid boiling at 305°, serving as a starting material in this paper.[2]

Formate, Acetate and Propionate.—Five grams of $(n\text{-}Pr_3Ge)_2O$ and 3.3 g. of 90% formic acid formed two layers when shaken, the lower layer being 0.5 ml., with a temperature rise of seven degrees; after a slow distillation of water and acid, 2.7 ml. of solution was condensed in a receiver, while 6.0 g. of product remained in the distillation unit (provided with ground joints, and accepting a thermometer with a ground joint). Table I lists the conditions of distillation of each new compound, and also properties and analyses of each compound. In every case except that of the acetate the center fraction of the new liquid was taken for study; with the acetate the last fraction was used.

4.60 g. of organogermanium oxide and 5.3 g. of glacial acetic acid ultimately furnished a nearly quantitative yield of the organogermanium acetate; the use of acetic anhydride is less satisfactory.

Two grams of propionic acid and 4.4 g. of organogermanium oxide, treated like the formate, finally gave a quantitative yield of ester.

Halogenoacetates.—Only the preparation of the trifluoroacetate was completely similar to that of the formate; 4.3 g. of organogermanium oxide and 3.4 g. of pure trifluoroacetic acid when mixed rose 17° in temperature spontaneously. After heating carefully for a few minutes, water drops separated out; purification was by distillation, with an essentially quantitative yield.

When 5.5 g. of organogermanium oxide and 3.4 g. of molten pure monochloroacetic acid reacted, with formation of water, caution was necessary, since such a mixture resembles cold water and hot oil—when one tried to distil out the water. After centrifugal separation of water, the monochloroacetate was distilled using an antifoam, and at 10 mm. Thus purified, the center fraction of the monochloracetate gave the expected neutralization equivalent, and contained no *hydrolyzable* chlorine. Yet when boiled for a few minutes at atmospheric pressure the originally colorless liquid had turned a light orange-yellow, and gave a strong positive test for *hydrolyzable* chlorine.

Three grams of dichloroacetic acid and 4.0 g. of organogermanium oxide reacted with formation of water, which could be distilled from the mixture at 20 mm. pressure; as distilled under reduced pressure, the center cut of the dichloroacetate contained no hydrolyzable chlorine. However, the boiling point at 760 mm. dropped 5° within two minutes of reflux, with formation of hydrolyzable chlorine.

Six grams of monobromoacetic acid and 3.2 g. of organogermanium oxide were warmed to 95° in a test-tube, whereby a little water escaped, but the bulk was removed by centrifuging. After distillation of excess acid at low pressure, then the monobromoacetate boiled at 147–150° in the center fraction; essentially no hydrolyzable bromine was present—pure bromoacetic acid and silver nitrate solution give a gray-black precipitate, probably silver. Moreover, the neutralization equivalent was satisfactory. When refluxed at 760 mm., the monobromoacetate darkened and contained hydrolyzable bromine. Yields of halogenoacetates were essentially quantitative.

Tri-*n*-propylgermanium iodoacetate should, by prediction, be not very stable. Tri-*n*-propylgermanium trichloroacetate was quite unstable.

Sulfate (by Transesterification).—Warming a mixture of 5.15 g. of pure tri-*n*-propylgermanium propionate and 0.71 g., a deficiency, of 100% sulfuric acid produced free propionic acid, 1.25 g. of which distilled over at 120–150° at 760 mm. Thereupon, after distillation of the excess of tri-*n*-propylgermanium propionate at approximately 122° under 12 mm., the bis-(tri-*n*-propylgermanium) sulfate was distilled at 1 mm. pressure, collecting a center fraction at 180–182°.

Other Studies of Transesterifications.—At this time it appeared highly desirable to explore the possibilities of transesterifications, which also could be called displacements or ester exchanges.

In the first observed transesterification, 2.82 g. of pure $Et_3Ge(OCOCH_3)$[1] and 0.53 g. of 100% sulfuric acid—a slight deficiency of acid—were mixed and then distillation over a 10-minute period yielded 0.68 g. of glacial acetic acid, b.p. 119° and n^{30} 1.372. Further distillation yielded a cut of 0.22 ml. at 100–180° under 80 mm. pressure, evidently

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[1] H. H. Anderson, THIS JOURNAL, **72**, 2089 (1950).

[2] H. H. Anderson, *ibid.*, **73**, 5440 (1951).

TABLE I

M.p. of the sulfate is approximately 35°. *n*-$Pr_3Ge(CCl_3COO)$ is unstable. RGe observed, formate to bromoacetate, respectively, 9.0, 8.7, 8.8, 9.6 (if RF is 1.0), 8.7, 9.1, 9.1. All distillations made at the lowest pressure in the Table.

Compound	B.p., °C.	Mm.	d^{20}_4	n^{20}	R	Mol. wt. Calcd.	Mol. wt. Found	Neut. equiva., g. Calcd.	Neut. equiva., g. Found
n-$Pr_3Ge(HCOO)$	233	760	1.094	1.4505	60.7	246.9	239	246.9	245, 246
	108–109	12							
n-$Pr_3Ge(CH_3COO)$	236	760	1.071	1.4464	65.0	260.9	251	260.9	257, 255
	112–113	13							
n-$Pr_3Ge(C_2H_5COO)$	246	760	1.054	1.4473	69.7	274.9	260	274.9	270.5, 271.5
n-$Pr_3Ge(CF_3COO)$	226	760	1.189	1.4103	65.7	314.9	306	314.9	313.5, 314
n-$Pr_3Ge(CH_2ClCOO)$	265 dec.	760	1.166	1.4640	69.9	295.4	280	295.4	295, 295.5
	143	10							
n-$Pr_3Ge(CHCl_2COO)$	266 dec.	760	1.226	1.4708	75.2	329.8	310	329.8	330.5, 329
	150	10							
n-$Pr_3Ge(CH_2BrCOO)$	267 dec.	760	1.325	1.4778	73.2	339.8	315	339.8	339, 338
	149	10							
(*n*-$Pr_3Ge)_2SO_4$	370	760	1.186	....	..	449.8	465	249.9	252, 256
	180–182	1	(40°)						

crude unchanged $Et_3Ge(OCOCH_3)$, and finally 1.9 ml. of a colorless liquid boiling at about 175° under 6 mm. pressure, later identified as $(Et_3Ge)_2SO_4$, from a n^{32} of 1.472 and an analysis SO_4 = 23.4. Thus the yield of organogermanium sulfate was quantitative, based upon available sulfate, and also the product compared quite favorably with that made from oxide and sulfuric acid.[3]

Five grams of pure tri-*n*-propylgermanium trifluoroacetate and 2.60 g. of pure trichloroacetic acid, when warmed gently for 10 minutes, gave a distillate at 70–80° of 1.65 g. of trifluoroacetic acid, as expected. Yet no definite, constant-boiling component could be detected in the residue, which boiled from 90 to 160° under 12 mm. pressure, and which contained hydrolyzable chlorine. In a related effort the organogermanium oxide and trichloroacetic acid furnished water, but preparations always contained hydrolyzable chlorine after heating.

Four other transesterifications are summarized by the equations

$$Pr_3Ge(OCOH) + CHCl_2COOH \longrightarrow Pr_3Ge(OCOCHCl_2) + HCOOH\uparrow$$

$$2Pr_3Ge(OCOCHCl_2) + H_2SO_4 \longrightarrow (Pr_3Ge)_2SO_4 + 2HOCOCHCl_2\uparrow$$

$$Pr_3Ge(OCOH) + CH_2ClCOOH \longrightarrow Pr_3Ge(OCOCH_2Cl) + HCOOH\uparrow$$

$$Et_3GeSCH_2COOGeEt_3 + H_2SO_4 \longrightarrow (Et_3Ge)_2SO_4 + HSCH_2COOH\uparrow$$

These reactions were performed on a scale of approximately 1 g. of the ester and a slight deficiency of the less volatile acid; characterization of the acid liberated depended on boiling point, refractive index and odor. It is best to use diminished pressure and equipment with ground joints.

Properties and Analyses of New Compounds; see Table I.—All the liquids are colorless, also probably soluble in a variety of organic liquids; the marked odors follow: formate, penetrating; acetate, camphoraceous, acidic; propionate, weakly acidic, then aromatic. Liquids of this class do not hydrolyze readily in water, because of insolubility; hydrolysis is rapid in 95% ethanolic sodium hyhydroxide solution, which served in the analysis aided by use of micropipets.[4,5]

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[3] H. H. Anderson, THIS JOURNAL, **72**, 194 (1950).

[4] H. H. Anderson, *ibid.*, **71**, 1801 (1949).

[5] H. H. Anderson, *Anal. Chem.*, **20**, 1241 (1948).