

TRIISOPROPYLGERMANIUM ESTERS

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A previous exploratory investigation of organogermanium esters established the method of transesterification in which the more volatile acid is distilled from the equilibrium mixture in a period of 15 minutes or less (1); the equilibrium is $R_3GeOCOR' + HOCOR'' \rightleftharpoons R_3GeOCOR'' + HOCOR'$. This publication included the straightforward preparation of four organogermanium haloacetates, $(n-C_3H_7)_3GeOCOCH_2Cl$, $(n-C_3H_7)_3GeOCOCH_2Br$, $(n-C_3H_7)_3GeOCOCHCl_2$, and $(n-C_3H_7)_3GeOCOCF_3$, believed to be the first volatile organogermanium haloacetates (1). Heating of 4.5 g. of $[(n-C_3H_7)_3Ge]_2O$ and 4.0 g. of CCl_3COOH at 90° produced water and a product containing no hydrolyzable chloride; however, removal of water by reflux resulted in the formation of much hydrolyzable chloride, indicating that "tri-*n*-propylgermanium trichloroacetate was quite unstable".

The present paper describes the preparation of triisopropylgermanium trichloroacetate, which was distilled under one-mm. pressure, but which decomposed readily before a boiling point under 760 mm. pressure could be measured. This paper also shows the decomposition of other esters of acids containing halogens; thermal decomposition of the β -chloropropionate, an ester of comparatively-low stability, yields propenoic acid and the corresponding organogermanium chloride: $(i-C_3H_7)_3GeOCOCH_2CH_2Cl \rightarrow (i-C_3H_7)_3GeCl + CH_2=CHCOOH$.

A previous paper reported the isolation of triisopropylgermanium hydroxide, produced by the hydrolysis of $(i-C_3H_7)_3GeBr$ (2); this paper listed six differences between tri-*n*-propylgermanium and di-*n*-propylgermanium compounds and the corresponding triisopropylgermanium compounds. Steric effects could have explained the differences between the *n*-propylgermanium and the isopropylgermanium derivatives; the chief differences were as follows: the failure of $i-C_3H_7MgCl$ to convert $GeCl_4$ into $(i-C_3H_7)_4Ge$; the existence of stable $(i-C_3H_7)_3GeOH$; the failure of acetic acid to convert $(i-C_3H_7)_3GeOH$ into a pure acetate, as mentioned in a single sentence (2).

Now, the present paper describes the successful preparation of fairly-pure triisopropylgermanium acetate, and rather-pure propionate, *n*-butyrate, and *n*-valerate, as well as a number of other esters. At present it is not possible to make a sound comparison of the stabilities of the corresponding tri-*n*-propylgermanium esters and the triisopropylgermanium esters.

In the reversible reaction $(i-C_3H_7)_3GeOH + HOCOR \rightleftharpoons (i-C_3H_7)_3GeOCOR + H_2O$ four or five steps probably are involved, the last of which is the elimination of water; only the strong acid CF_3COOH has given pure esters this way (H_2SO_4 does also). Fairly-strong α -halo acids such as $CH_2ClCOOH$ yield pure esters this way if anhydrous sodium sulfate is present as an acceptor for the

water formed in the reaction, or if the water can be removed by centrifuging and pipetting. As a whole, the *irreversible* reaction $(i\text{-C}_3\text{H}_7)_3\text{GeCl} + \text{AgOCOR} \rightarrow (i\text{-C}_3\text{H}_7)_3\text{GeOCOR} + \text{AgCl}$ is the best method from a statistical viewpoint, since it is applicable to the preparation of esters of *weak* organic acids. For the time being, it seems most probable that an acid reacts through formation of an —OCOR ion, which makes the attack, while a silver salt probably reacts through formation of an Ag^+ ion, which then makes the attack.

Organometallic trifluoroacetates seem unusually stable when compared with other organometallic haloacetates and halopropionates. This stability of trifluoroacetates appears mainly due to the stability of the C—F bond, known to be very high.

EXPERIMENTAL

This article includes the preparation of 15 new triisopropylgermanium derivatives. Because of the low stability of many esters the article presents fairly-complete information concerning the preparation of many esters.

Starting materials included $(i\text{-C}_3\text{H}_7)_3\text{GeOH}$ (2); commercial silver acetate; carefully prepared silver propionate, silver *n*-butyrate, silver *n*-valerate, silver monochloroacetate, silver α -chloropropionate, silver β -chloropropionate, silver benzoate, and silver cyanate; Eastman Kodak halo acids, several of which required removal of water absorbed from the air; and 100% sulfuric acid. In the typical preparation of a silver salt other than the cyanate, a given amount of the free organic acid was neutralized with sodium hydroxide solution; then the solution was made slightly acid with nitric acid and the silver salt was precipitated. Silver salts which contained halogen were allowed to stand about 20 minutes, then washed successively with 50% ethanol, 75% ethanol, 95% ethanol, and finally ether; and finally dried in air at 25°. Washing of the α -chloropropionate, a fairly-soluble, crystalline salt, was by decantation.

Borosilicate glass equipment, with standard-taper ground joints, served in all reactions and purifications. Self-adjusting (in the final stage) micropycnometers aided in the determinations of density; self-filling micropipets allowed easy, accurate determination of the acidity by measuring liquids and later titrating with sodium hydroxide (3) in 95% ethanolic solution.

I. REACTIONS USING SILVER SALTS

Triisopropylgermanium acetate. In the absence of a solvent exactly 3 g. of $(i\text{-C}_3\text{H}_7)_3\text{GeCl}$ and 4.5 g. of silver acetate were allowed 30 minutes of reflux, and then the organogermanium fraction was distilled under 100 mm. pressure and collected in a small distilling unit. Redistillation of the 3.1 g. yield—a yield of 90%—involved rejection of the lowest-boiling 30%, followed by collection of a fraction for study. This ester was clear, colorless, of normal viscosity, and with a primarily camphoraceous odor. Table I lists the other properties.

Triisopropylgermanium propionate. Exactly as with the acetate above, reaction of exactly 2 g. of triisopropylgermanium chloride and 3.20 g. of silver propionate furnished a nearly-quantitative yield of triisopropylgermanium propionate, a liquid of less pronounced odor than that of the acetate.

Triisopropylgermanium n-butyrate. Just as with the acetate above, 15 minutes reflux of exactly 1.5 g. of triisopropylgermanium chloride and 2.20 g. of silver *n*-butyrate furnished triisopropylgermanium *n*-butyrate in essentially quantitative yield—almost 2.0 g. A neutralization equivalent of 273 indicated presence of a little free *n*-butyric acid. Reflux of the liquid with 0.07 g. of dry potassium hydroxide in five small pieces yielded a product with neutralization equivalent of 280, which was given one more minute of reflux with the base. When a new center fraction was collected, the new neutralization equivalent indicated a

rather pure product, which had practically no odor, but seemed to be of a little more than ordinary viscosity.

Triisopropylgermanium n-valerate. After one hour of reflux in 8 ml. of carbon tetrachloride, exactly 2 g. of triisopropylgermanium chloride and 2.5 g. of silver *n*-butyrate yielded, after filtration and washing of the silver salts, 2.34 g. of triisopropylgermanium *n*-valerate. Chloride-free, the product represented a yield of 93% ,with a viscosity a little more than that of carbon tetrachloride.

Triisopropylgermanium monochloroacetate. Fifteen minutes reflux, under 100 mm. pressure without a solvent, of exactly 3 g. of silver monochloroacetate and 2 g. of triisopropylgermanium chloride was followed by total distillation of the resulting liquid under one mm. pressure. Redistillation under one mm. pressure yielded a center fraction of very little odor, more than ordinary viscosity, and containing a small amount of free monochloroacetic acid, but only a trace of hydrolyzable chloride. The monochloroacetate did not darken during reflux under 760 mm., and only a trace of hydrolyzable chloride was present afterwards.

Triisopropylgermanium β -chloropropionate. Thirty minutes reflux, in 9 ml. of carbon tetrachloride, of exactly 2 g. of triisopropylgermanium chloride and 2.6 g. of silver β -chloropropionate, followed by filtration and washing of the silver salts, yielded 2.33 g. of triisopropylgermanium β -chloropropionate, a yield of 89%. Distillation under one mm. pressure yielded a fairly pure center fraction. In an unexpectedly fast drop in apparent boiling point the highest readable reflux temperature dropped from 246° to 225° within one minute—the thermometer bulb was in the heated liquid. Much hydrolyzable chloride formed, and the decomposition was probably the most rapid yet observed for an organometallic ester containing halogen. There is an account of the reaction products of this decomposition in a later section of this paper, IV. DECOMPOSITION OF HALOACETATES AND HALOPROPIONATES.

Triisopropylgermanium α -chloropropionate. After one hour of reflux in 8 ml. of carbon tetrachloride, followed by filtration and washing of the silver salts, exactly 2 g. of triisopropylgermanium chloride and 2.54 g. of silver α -chloropropionate furnished 2.13 g. of triisopropylgermanium α -chloropropionate. Upon fractional distillation the center half was collected for study. The over-all yield of ester was 81%, the material containing only a slight trace of hydrolyzable chloride. This isomer is much more stable to heat than is the β -chloropropionate.

Triisopropylgermanium benzoate. Ten minutes free reflux of 2.10 g. of triisopropylgermanium chloride and 3.30 g. of silver benzoate without a solvent (perhaps a longer reflux in 9 ml. of carbon tetrachloride would have been preferable) was followed by distillation under one mm. pressure, later followed by redistillation under one mm. with collection of a viscous, colorless, liquid center fraction for study.

Triisopropylgermanium (iso)cyanate. Forty minutes *gentle* reflux of 3.00 g. of triisopropylgermanium chloride and 2.40 g. of silver cyanate without a solvent was followed by total distillation of the liquid under 70 mm. pressure, and then fractional distillation under one mm. pressure. Chloride was absent from the mobile liquid cyanate. An overall amount of 2.94 g. of the liquid cyanate represented a yield of 96%.

II. REACTIONS USING ACIDS

Triisopropylgermanium trifluoroacetate. Mixture of 4.00 g. of triisopropylgermanium hydroxide and 4.2 g. of trifluoroacetic acid produced a temperature rise of approximately 10°, accompanied by formation of an emulsion containing water. After a few minutes of reflux the mixture of acid and water was distilled, leaving 5.53 g. of triisopropylgermanium trifluoroacetate, a yield of 96%. Next, fractional distillation followed, with rejection of the lowest boiling 30%, and collection of all except the last 10% for study. This trifluoroacetate is a clear, colorless, mobile liquid, with a primarily camphoraceous odor.

Bis-(triisopropylgermanium) sulfate. Reflux of 4.3 g. of triisopropylgermanium hydroxide and 4.4 g. of glacial acetic acid, even followed by reflux with acetic anhydride for an hour, failed to furnish a pure acetate upon careful fractional distillation; the observed neutrali-

zation equivalent was 282. Probably 5% of impurities such as organogermanium oxide or hydroxide was present. However, 15 minutes gentle reflux of 3.75 g. of crude triisopropylgermanium acetate and 0.53 g. of 100% sulfuric acid furnished 0.60 g. of glacial acetic acid as a distillate. Further distillation, under 90 mm. pressure allowed escape of a little more acetic acid and most of the excess triisopropylgermanium acetate. Still further distillation, under one mm. pressure, separated the 2.4 g. yield of organogermanium sulfate into a 0.4-g. low fraction and a 2.0-g. fraction collected for study. This 2.0-g. fraction had a viscosity much like that of sulfuric acid.

Triisopropylgermanium dichloroacetate. A mixture of 2.15 g. of triisopropylgermanium hydroxide and 1.31 g. of dichloroacetic acid (a very slight excess of acid) upon combination furnished an immediate opalescence. After heating at 95° for 10 minutes, with stirring, the mixture was then cooled to 25° and centrifuged; next, the 0.17 ml. of water present was pipetted off. After drying with sodium sulfate, the compound was transferred to distilling equipment and the solid was washed with (30–60°) petroleum ether. Distillation of the solvent under 80 mm. pressure was followed by fractional distillation of the ester under one mm. pressure, with rejection of the first 0.6 ml., then collection of 1.6 ml. for study, leaving 0.5 ml. in the distilling unit. Thus the yield was essentially quantitative. This compound forms hydrolyzable chloride slowly at 275°.

Triisopropylgermanium trichloroacetate. Heating a mixture of 1.23 g. of triisopropylgermanium hydroxide and 0.90 g. of dry trichloroacetic acid for 10 minutes at 90° produced water quickly. After cooling to 25°, the lower layer (ester) was removed by pipet. Fractional distillation under one mm. pressure followed, with rejection of the first 0.60 ml. and then collection of 0.90 ml. for study. Hydrolyzable chloride was absent. No true boiling point under 760 mm. could be determined, since the compound turned a medium red, the reflux temperature dropped visibly, and hydrolyzable chloride formed rapidly. The yield was essentially quantitative.

Triisopropylgermanium iodoacetate and triisopropylgermanium bromoacetate. In practically the same manner as with the trichloroacetate above, 1.94 g. of triisopropylgermanium hydroxide and 1.62 g. of iodoacetic acid (a slight deficiency of acid) gave a nearly quantitative yield of ester. In fractional distillation, the first 0.65 ml. was rejected, then the next 1.40 ml. was collected for study, while a 0.3-ml. residue remained in the distilling unit. Reflux of the organogermanium iodoacetate in air resulted in formation of some free iodine, with a gradual drop in boiling point. Similarly, heating 2.15 g. of triisopropylgermanium hydroxide with 1.39 g. of bromoacetic acid yielded a 0.8-ml. low fraction, then a 1.40-ml. center fraction for study, and a 0.35-ml. residue—a nearly quantitative over-all yield. At the boiling point under 760 mm. pressure the bromoacetate formed hydrolyzable bromide rapidly and the observed boiling point dropped about 4°/minute.

III. PHYSICAL PROPERTIES: SEE TABLE I

Table I lists the chief properties and the analyses of the pure compounds. In many instances esters containing halogen decomposed rapidly enough to make the reported boiling point only approximate under 760 mm. pressure; in some instances it was impossible to find boiling points under 760 mm. pressure. Measurements were on the day of purification.

IV. DECOMPOSITION OF HALOACETATES AND HALOPROPIONATES

These triisopropylgermanium haloacetates and halopropionates decomposed in approximately the same relative degree of ease as the corresponding free acids do. The trifluoroacetate was highly stable; the bromoacetate and especially the iodoacetate were relatively unstable; the β -chloropropionate was much less stable than the α -chloropropionate.

Decomposition of the β -chloropropionate. After seven minutes of reflux, 1.0 ml. of the decomposed ester was transferred to a microdistillation unit. Fractional distillation under 760 mm. pressure furnished four separate fractions as follows: low fraction, 0.20-ml. volume, true b.p. 143°, density 1.08, n_D^{20} 1.443, with a little white polymer present, also neutraliza-

TABLE I
 PROPERTIES OF TRIISOPROPYLGERMANIUM ESTERS

Compound	B.P., ^a °C	mm.	d_4^{20}	n_D^{20}	R	Mol. Wt.		Neut. Equiv.	
						Calc'd	Found	Calc'd	Found
$(i-C_3H_7)_3GeOCOCH_3$	229	760	1.070	1.453 ₂	65.9	260.9	255	260.9	268, 269
	152-153	83							
$(i-C_3H_7)_3GeOCOC_2H_5$	242	760	1.059	1.453 ₈	70.3	274.9	265	274.9	275, 275
	164-166	90							
$(i-C_3H_7)_3GeOCO-n-C_4H_9$	256	760	1.045	1.548 ₀	75.4	288.9	272	288.9	288, 289
	180-182	98							
$(i-C_3H_7)_3GeOCO-n-C_4H_9$	266	760	1.034	1.456 ₀	79.6	303.0	300	303.0	303, 303
	82-83	1							
$(i-C_3H_7)_3GeOCOCH_2Cl$	269	760	1.182	1.472 ₂	70.0	295.4	273	295.4	290, 291
	101-103	1							
$(i-C_3H_7)_3GeOCOCHCl_2$	275	760	1.236	1.477 ₂	75.4	329.8	320	329.8	332, 330
	92-93	1							
$(i-C_3H_7)_3GeOCOCCl_3$	107-109	1	1.291	1.485 ₀	80.9	364.3	356	364.3	363, 236
	220	760	1.178	1.420 ₀	67.6	314.9	300	314.9	313, 112
$(i-C_3H_7)_3GeOCOCH_2Br$	271 dec	760	1.331	1.487 ₂	73.5	339.8	320	339.8	340, 340
	98-99	1							
$(i-C_3H_7)_3GeOCOCH_2I$	281	760	1.465	1.509 ₀	78.8	386.8	374	386.8	388, 384
	107-108	1							
$(i-C_3H_7)_3GeOCOCH_2CH_2Cl$	97-99	1	1.154	1.471 ₇	75.0	309.4	302	309.4	306, 305
	269	760	1.144	1.467 ₂	75.3	309.4	302	309.4	308, 307
$(i-C_3H_7)_3GeOCOCHClCH_3$	95-97	1							
	317	760	1.132	1.513 ₈	85.9	323.0	334	323.0	315, 316
$(i-C_3H_7)_3GeOCOCH_2H_2$	130-132	1							
	238	760	1.097	1.460 ₂	61.1	243.9	250	243.9	241, 241
$(i-C_3H_7)_3Ge(NCO)$	65-66	1							
	380	760	1.217	1.482	117.1	499.8	465	249.9	247, 246
$[(i-C_3H_7)_3Ge]_2SO_4$	182-184	1							

^a Distillation of each compound at the lowest pressure listed.

tion equivalent 109, also some unsaturation to bromine in carbon tetrachloride, also with an odor like that of propionic acid (this fraction was propenoic acid, partly polymerized); *center* fraction, b.p. 186-212°, evidently a mixture, 0.3 ml. in volume; *high* fraction, 0.3 ml. in volume, with b.p. 222°, n_D^{20} 1.471, d_4^{20} 1.119, neutralization equivalent 246, also a chloride [this is crude triisopropylgermanium chloride (2)]; a *residue*, 0.15 ml., partly dark-colored. Integration of this information leads to the conclusion that triisopropylgermanium chloride and propenoic acid are the primary decomposition products, while propenoic acid polymerizes in part later.

SUMMARY

1. Triisopropylgermanium hydroxide reacts easily with the strong acids trifluoroacetic acid and sulfuric acid to yield the corresponding esters, $(i-C_3H_7)_3GeOCOCF_3$ and $[(i-C_3H_7)_3Ge]_2SO_4$. However, triisopropylgermanium hydroxide and weak organic acids such as formic or acetic do not yield pure esters. This behavior is surprisingly unlike that of $[(n-C_3H_7)_3Ge]_2O$, which reacts with acetic acid to furnish a pure ester.

2. Rather pure triisopropylgermanium acetate results in the reaction of silver acetate and the apparently sterically-hindered triisopropylgermanium chloride—which reacts no further with excess isopropylmagnesium chloride.

3. Fifteen new triisopropylgermanium derivatives, reported herein, include the following: $(i-C_3H_7)_3GeOCOCH_3$, $(i-C_3H_7)_3GeOCOC_2H_5$, $(i-C_3H_7)_3GeOCO-n-$

C_3H_7 , $(i-C_3H_7)_3GeOCO-n-C_4H_9$, $(i-C_3H_7)_3GeOCOCH_2Cl$, $(i-C_3H_7)_3GeOCOCHCl_2$, $(i-C_3H_7)_3GeOCOCCl_3$, $(i-C_3H_7)_3GeOCOCF_3$,¹ $(i-C_3H_7)_3GeOCOCH_2Br$, $(i-C_3H_7)_3GeOCOCH_2I$, $(i-C_3H_7)_3GeOCOCH_2CH_2Cl$, $(i-C_3H_7)_3GeOCOCHClCH_3$, $(i-C_3H_7)_3GeOCOC_6H_5$, $(i-C_3H_7)_3Ge(NCO)$, and $[(i-C_3H_7)_3Ge]_2SO_4$.

4. Among the esters derived from halogenated organic acids, only $(i-C_3H_7)_3GeOCOCF_3$ is fully stable at its boiling point under 760 mm. Experimental evidence indicates that the thermal decomposition of the β -chloropropionate yields propenoic acid and the corresponding organogermanium chloride: $(i-C_3H_7)_3GeOCOCH_2CH_2Cl \rightarrow (i-C_3H_7)_3GeCl + CH_2=CHCOOH$.

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