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TRIETHYLGERMANIUM HALOACETATES AND HALOPROPIONATES

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One of the earliest papers on organogermanium esters (1) reported the preparation of $(C_2H_5)_3GeOCOH$, $(C_2H_5)_3GeOCOCH_3$, $(C_2H_5)_3GeOCOCH_2SGe(C_2H_5)_3$, $(C_2H_5)_2Ge(OCOH)_2$, and $(C_2H_5)_2Ge(OCOCH_3)_2$, all made from the appropriate ethylgermanium oxide and the appropriate organic acid.

The present paper reports eleven triethylgermanium haloacetates and halopropionates, also the propionate, *n*-butyrate, and *n*-valerate. Many of the preparative methods are now different from the early procedures (1), in order to overcome numerous experimental difficulties.

A recent publication on triisopropylgermanium esters (2) demonstrates preparation of organogermanium halopropionates through reaction of a trialkylgermanium halide with a silver chloropropionate; it also demonstrates preparation of organogermanium haloacetates through reaction of a trialkylgermanium acetate with a haloacetic acid.

The present paper includes four trans-esterifications based on a published method (3) of distilling the more volatile acid from the equilibrium $R_3GeOCOR' + HOCOR'' \rightleftarrows R_3GeOCOR'' + HOCOR'$.

Upon comparing the information now available on organogermanium haloacetates and halopropionates (2, 3), including the present paper, certain trends in resistance to the formation of hydrolyzable halide are apparent if we consider rates of formation of hydrolyzable halide at the boiling point of each compound at atmospheric pressure. *First*, in the chloroacetates the greater the chlorine content, the more rapid the formation of hydrolyzable chlorine; trialkylgermanium trichloroacetates decompose so rapidly that their distillations must be at 3 mm. pressure or less; dichloroacetates form hydrolyzable chlorine less rapidly, while chloroacetates with one chlorine yield hydrolyzable chlorine most slowly of all. *Second*, keeping the same halogen, say bromine, and the same organogermanium configuration, $R_3GeOCOCH_2CH_2Br$ forms hydrolyzable bromine more rapidly than does $R_3GeOCOCHBrCH_3$, which forms hydrolyzable bromine more rapidly than does $R_3GeOCOCH_2Br$; chloroesters behave similarly. *Third*, taking the $R_3GeOCOCH_2X$ type of haloester for example, the iodoester forms hydrolyzable halide more rapidly than does the bromoester, which forms hydrolyzable halide more rapidly than does the chloroester, while no decomposition of a fluoroester is yet known; the trend is in the same direction for the $R_3GeOCOCH_2CH_2X$ type, which in one case (2) forms propenoic acid as one of the decomposition products.

These trends in decomposition seem closely related to the ease of decomposition of each free acid.

EXPERIMENTAL

This article includes the preparation of fourteen previously unreported triethylgermanium esters, eleven of which contain halogen or a cyano group. There is a description of typical preparations and a listing of the starting quantities for most other preparations.

Starting materials included pure $(C_2H_5)_3GeOGe(C_2H_5)_3$ (1, 4) and $(C_2H_5)_3GeBr$ made therefrom using hydrobromic acid, and also $(C_2H_5)_3GeOCOCH_3$, made from the organogermanium oxide and acetic acid; dry silver *n*-valerate, silver α-chloropropionate and silver β-chloropropionate (2); Eastman Kodak white label haloacids, some of which required removal of water absorbed from the air.

Equipment included borosilicate glassware with standard taper ground joints; micropycnometers that were self-adjusting in the last stage of filling; self-filling micropipets for the accurate determination of acidity by measuring the pure liquid and then titrating with sodium hydroxide in 95% ethanol.

I. REACTIONS USING SILVER SALTS

Triethylgermanium α-chloropropionate. After one hour of reflux of 2.83 g. of $(C_2H_5)_3GeBr$ and 3.5 g. of $AgOCOCHClCH_3$ in 8 ml. of CCl_4, the mixture was filtered with washing of the silver salts. Distillation of solvent followed, partly under 80 mm. pressure. A yield of 3.13 g. of $(C_2H_5)_3GeOCOCHClCH_3$ was nearly quantitative; in fractional distillation under one mm. pressure the lowest-boiling 0.72 g. was set aside and the center 0.96 g. collected for study, while a residue of 1.45 g. remained in the distilling unit. No hydrolyzable halide was present in the clear, mobile center fraction. *Preparation of the other isomer* involved identical starting amounts and a comparable procedure; the yield of ester was 2.90 g., the center-boiling 1.55 g. of which served for study.

Triethylgermanium n-valerate resulted in a similar procedure using 2.83 g. of $(C_2H_5)_3GeBr$ and 3.35 g. of silver *n*-valerate; 2.76 g. of ester obtained amounted to a yield of 90%. In fractional distillation under one mm. pressure the lowest-boiling 0.85 g. was set aside and the next 1.40 g. collected for study. This ester had only a faint odor of valeric acid; it was clear, colorless and free of halogen.

II. REACTION OF TRIETHYLGERMANIUM ACETATE WITH ACIDS

Triethylgermanium β-bromopropionate. Ten minutes gentle reflux of 2.55 g. of $(C_2H_5)_3GeOCOCH_3$ and 1.53 g. of $BrCH_2CH_2COOH$ yielded 0.63 g. of CH_3COOH distilled chiefly at 90° under 150 mm. pressure. Next, distillation under 34 mm. pressure furnished approximately 0.22 g. boiling at about 110°, chiefly excess $(C_2H_5)_3GeOCOCH_3$. Further distillation, under one mm. pressure, probably resulted in some loss of uncondensed products, but furnished first 0.97 g. boiling at 82–85°, and finally an end fraction of 1.86 g. boiling at 85–86° with the properties listed in Table I. If based on available $BrCH_2CH_2COOH$ the yield was 90%. In this trans-esterification a clean-cut separation of compounds was indispensable, and a little loss of material was unimportant.

Triethylgermanium α-bromopropionate. This preparation was almost identical to the above in amounts and procedure; however, the desired ester contained a little $(C_2H_5)_3GeOGe(C_2H_5)_3$, formed presumably by the action of a little water in the liquid $CH_3CHBrCOOH$. Treatment of 3.00 g. of crude $(C_2H_5)_3GeOCOCHBrCH_3$ with 0.25 g. of CH_3COOH formed low-boiling $(C_2H_5)_3GeOCOCH_3$, which was easily separable by distillation under 8 mm. pressure (b.p. about 90°). Further distillation under one mm. pressure yielded an end fraction of 1.60 g. with the properties in Table I.

Triethylgermanium β-iodopropionate. In the same process as used for triethylgermanium β-bromopropionate above, 2.55 g. of $(C_2H_5)_3GeOCOCH_3$ and 2.00 g. of ICH_2CH_2COOH furnished 3.40 g. of $(C_2H_5)_3GeOCOCH_2CH_2I$, a yield of 95%; the highest-boiling 2.1 g. served for study.

Triethylgermanium cyanoacetate. Similarly, 2.55 g. of $(C_2H_5)_3GeOCOCH_3$ and 0.84 g. of $CNCH_2COOH$ furnished approximately 2.2 g. of $(C_2H_5)_3GeOCOCH_2CN$, a yield of almost 90%. A residue of 0.18 g. was light-orange in color, but the highest-boiling 1.2 g. was colorless and contained no hydrolyzable cyanide in a short test.

III. BIS-(TRIETHYLGERMANIUM) OXIDE AND ACIDS

This method is useful when there is an ample difference in the boiling points of the compounds involved; it is advisable to have a 10–15% excess of the acid used, to ensure

TABLE I

PROPERTIES OF TRIETHYLGERMANIUM HALOACETATES AND HALOPROPIONATES

Compound	B.P.,[a] °C.	MM.	d_4^{20}	n_D^{20}	R	Mol. wt.		Neut. Equiv.	
						Calc'd	Found	Calc'd	Found
$(C_2H_5)_3GeOCOCH_2Cl$	234	760	1.243	1.467_2	56.6	253.3	252	253.3	255, 254
	113–114	6							
$(C_2H_5)_3GeOCOCHCl_2$	248	760	1.304	1.467_2	61.2	287.7	281	287.7	295, 294
	105–106	1							
$(C_2H_5)_3GeOCOCCl_3$	125–126	3	1.368	1.479_0	66.8	322.2	335	322.2	320, 321
$(C_2H_5)_3GeOCOCH_2Br$	244	760	1.423	1.484_2	59.9	297.7	292	297.7	301, 302
	74–75	1							
$(C_2H_5)_3GeOCOCH_2I$	254	760	1.593	1.511_2	63.0	344.7	338	344.7	346, 345
	85–86	1							
$(C_2H_5)_3GeOCOCH_2CN$	98–99	1	1.194	1.464	56.3	243.8	249	243.8	251, 251
$(C_2H_5)_3GeOCOC_2H_5$	205	760	1.109	1.448_1	56.2	232.9	228	232.9	236, 236
	119–120	50							
$(C_2H_5)_3GeOCO\text{-}n\text{-}C_3H_7$	221	760	1.084	1.448_6	61.0	246.9	252	246.9	248, 249
	133–134	47							
$(C_2H_5)_3GeOCO\text{-}n\text{-}C_4H_9$	230	760	1.062	1.446_7	65.6	260.9	257	260.9	259, 260
	62–63	1							
$(C_2H_5)_3GeOCOCHClCH_3$	235	760	1.201	1.461_9	61.2	267.3	253	267.3	266, 267
	73–75	1							
$(C_2H_5)_3GeOCOCH_2CH_2Cl$	236	760	1.210	1.467_2	61.3	267.3	255	267.3	263, 264
	74–75	1							
$(C_2H_5)_3GeOCOCHBrCH_3$	74–75	1	1.370	1.472_5	63.8	311.8	300	311.8	313, 309
$(C_2H_5)_4GeOCOCH_2CH_2Br$	85–86	1	1.376	1.483_2	64.7	311.8	298	311.8	311, 312
$(C_2H_5)_3GeOCOCH_2CH_2I$	94–96	1	1.544	1.500_2	68.4	358.8	340	358.8	352, 354

[a] Distillation of each compound at the lowest pressure listed.

complete reaction of the organogermanium oxide. Use of anhydrous sodium sulfate as an acceptor for the water formed in the individual reaction is far superior to removal of water by distillation (3).

Triethylgermanium monochloroacetate, triethylgermanium dichloroacetate and triethylgermanium trichloroacetate. Typically, combination of 2.30 g. of $(C_2H_5)_3GeOGe(C_2H_5)_3$ and 1.50 g. of *dry* $CH_2ClCOOH$—13.7 and 15.9 milliequivalents respectively—produced a cloudiness due to water in short order; after heating at 100° for 10 minutes, with mixing, the liquid was let cool to room temperature. After centrifuging, a large proportion of the water formed was removed by micropipet; the remainder of the water was removed by allowing to stand 3 hours with Na_2SO_4. Next, the main body of the ester was transferred to a distilling unit using a transfer pipet; 0.6 ml. of (30–60°) petroleum ether was used in washing the Na_2SO_4. After distillation of the petroleum ether, the ester was distilled; at first the mixture contained 3.4 g. of ester and 0.27 g. of excess $CH_2ClCOOH$—or a practically quantitative yield of the ester. After distillation of 1.35 g. of material boiling below 148° under 52 mm. pressure (0.27 g. of this was excess $CH_2ClCOOH$), a center fraction of 1.75 g. of $(C_2H_5)_3GeOCOCH_2Cl$ was collected for study using the conditions listed in Table I; a residue of 0.5 g. remained in the distilling unit. Because of limited stability, the trichloroacetate was distilled at 3 mm. pressure following removal of the petroleum ether under low pressure.

Triethylgermanium bromoacetate and triethylgermanium iodoacetate. These preparations resembled those of the chloroacetates above, with all distillations under one mm. pressure; however, it was not easy to remove excess acid from the esters. As judged by altered preparative methods, the best way to make an ester like these is to treat the organogermanium oxide with a deficiency of haloacid and then to give the crude ester a second treatment with a slight excess of acetic acid. When an ester contains excess bromoacetic acid or excess iodoacetic acid, then organogermanium oxide and acetic acid are added in small amounts, followed by gentle reflux for one minute and then fractional distillation under low pressure.

Triethylgermanium propionate and triethylgermanium n-butyrate. In these preparations the chloroacetate method above sufficed, with conditions of distillation listed in Table I. Perhaps the use of silver salts would have given slightly purer products.

IV. DECOMPOSITION OF HALOACETATES AND HALOPROPIONATES

Even at the b.p. under 760 mm. pressure $(C_2H_5)_3GeOCOCH_2Cl$ formed no hydrolyzable chloride in 2 minutes; $(C_2H_5)_3GeOCOCHCl_2$ seemed to form a very small amount of hydrolyzable chloride; in contrast, $(C_2H_5)_3GeOCOCCl_3$ formed hydrolyzable chloride so rapidly at the b.p. under 760 mm. pressure that even a rough estimate of the b.p. was impossible.

At the b.p. under 760 mm. pressure $(C_2H_5)_3GeOCOCH_2Br$ presented no difficulties; $(C_2H_5)_3GeOCOCH_2I$ turned light-purple; $(C_2H_5)_3GeOCOCH_2CN$ turned medium-orange at the apparent b.p. of 235°.

At the b.p. under 760 mm. pressure $(C_2H_5)_3GeOCOCH_2CH_2Cl$ forms hydrolyzable chloride more rapidly than does $(C_2H_5)_3GeOCOCHClCH_3$; the b.p.s are fairly exact. The corresponding bromoesters form hydrolyzable halide more rapidly; 3 minutes reflux of $(C_2H_5)_3GeOCOCH_2C_2HBr$ lowers the apparent b.p. from 226° to 198°, with formation of very much hydrolyzable bromide; $(C_2H_5)_3GeOCOCHBrCH_3$ has an apparent b.p. of about 240°, with formation of much hydrolyzable bromide. Under 760 mm. pressure heated liquid $(C_2H_5)_3GeOCOCH_2CH_2I$ reaches a maximum temperature of 225° and no b.p. can be measured because of very fast decomposition.

In the recent publication on triisopropylgermanium esters (2) an experiment showed the decomposition of a chloropropionate according to the reaction $(i\text{-}C_3H_7)_3GeOCOCH_2CH_2Cl \rightarrow (i\text{-}C_3H_7)_3GeCl + CH_2{=}CHCOOH$. Perhaps the decomposition involved the primary formation of $(i\text{-}C_3H_7)_3GeOCOCH{=}CH_2$ and HCl, and then the cleavage of the $(i\text{-}C_3H_7)_3GeOCOCH{=}CH_2$ by the HCl, which is a stronger acid than propenoic acid. Probably all the decompositions of halopropionates in the present article are similar, with formation of $CH_2{=}CHCOOH$.

Past efforts to show the identity of the decomposition products of organogermanium haloacetates (2, 3) were unsuccessful, although future efforts may prove adequate.

SUMMARY

1. Fourteen previously unreported triethylgermanium derivatives include the following $(C_2H_5)_3GeOCOCH_2Cl$, $(C_2H_5)_3GeOCOCHCl_2$, $(C_2H_5)_3GeOCOCCl_3$, $(C_2H_5)_3GeOCOCH_2Br$, $(C_2H_5)_3GeOCOCH_2I$, $(C_2H_5)_3GeOCOCH_2CN$, $(C_2H_5)_3GeOCOC_2H_5$, $(C_2H_5)_3GeOCO\text{-}n\text{-}C_3H_7$, $(C_2H_5)_3GeOCO\text{-}n\text{-}C_4H_9$, $(C_2H_5)_3GeOCOCHClCH_3$, $(C_2H_5)_3GeOCOCH_2CH_2Cl$, $(C_2H_5)_3GeOCOCHBrCH_3$, $(C_2H_5)_3GeOCOCH_2CH_2Br$, and $(C_2H_5)_3GeOCOCH_2CH_2I$.

2. There is a comparison of the rates of formation of hydrolyzable halogen by individual haloacetates and halopropionates at the boiling points under 760 mm. pressure. Iodo compounds form hydrolyzable halogen more rapidly than do bromo compounds, which in turn form hydrolyzable halogen more rapidly than do chloro compounds; there is no evidence yet of the formation of hydrolyzable halogen by any ester containing fluorine. Moreover, the haloester $R_3GeOCOCH_2CH_2X$ forms hydrolyzable halogen more rapidly than does the isomeric $R_3GeOCOCHXCH_3$.

3. Five of the eleven haloesters require distillation under 3 mm. pressure, or less, to avoid decomposition.

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