

Di-*n*-propylgermanium Diacetate.—Upon reflux for three hours and then distillation of excess anhydride, 3.5 g. of the oxide and 4.5 g. of acetic anhydride gave a 90% yield of the diacetate.

Di-*n*-propylgermanium Bis-(monochloroacetate).—Upon refluxing 3.60 g. of the diacetate and 2.50 g. of monochloroacetic acid at 43 mm. pressure, 1.55 ml. of crude acetic acid distilled. When distilled at very low pressure the center fraction of the resultant monochloroacetate contained no hydrolyzable chlorine; boiling at 760 mm. darkens the product and gives a positive test for hydrolyzable chlorine.⁴

Dimeric Di-*n*-propylgermanium Sulfate.—Heating 0.74 g. of 100% sulfuric acid and 3.05 g. (10% excess) of di-*n*-propylgermanium bis-(monochloroacetate) at a pressure of 17 mm. yielded as distillate 1.28 g. of monochloroacetic acid, a displacement of 90%. Recrystallization of the white solid residue from benzene, and then washing with petroleum ether followed; a second recrystallization furnished long, slender, colorless or white needles of the dimeric sulfate. The solubility of the easily hydrolyzed compound in benzene is 18 g./liter at 27° and over 90 g./liter at 70°.

Table I lists the properties of the compounds, all of which were center fractions obtained in equipment bearing ground joints. Analysis was based on titration primarily.

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Monoethylgermanium and Alkylsilicon Esters. Dimethylgermanium Diacetate

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Organogermanium oxides of the type $(R_3Ge)_2O$ or $(R_2GeO)_3$ or $_4$ react with acetic anhydride to yield the corresponding monoacetate or diacetate, respectively, but the oxide $[(RGeO)_2O]_n$ does not react with acetic anhydride.² Although anhydrous sodium acetate and alkylchlorosilanes furnish alkylacetoxysilanes with yields of approximately 50%, this³ method is less desirable for precious germanium compounds than the use of silver, lead or thallos salts, which are more covalent than the corresponding sodium salts. Tri-*n*-propylbromosilane and silver acetate yielded tri-*n*-propylacetoxysilane,⁴ while thallos acetate⁵ and germanium tetrachloride reacted in acetic anhydride furnishing germanium tetraacetate, m.p. 156°; probably the chief advantages of the anhydride were repression of hydrolysis and easy solution of germanium tetraacetate. Solvolysis⁶ may not be so important as the authors feel.

Lead formate is a suitable reagent for preparing some formates, but not for others; organogermanium formates are not all completely stable, since ethylgermanium triformate loses water and carbon monoxide, and has no definite b.p. at 760 mm. Lead formate and $MeSiI_3$ yielded no stable product, although they reacted. Therefore formate stabilities apparently increase from silicon to lead, and from triformate to monoformate. Di-*n*-propylgermanium diiodide and lead formate did not react; previously² diethylgermanium oxide and formic acid gave a 30% yield, while bis-(triethylgermanium) oxide and formic acid gave a 90%

yield. Perhaps silicon is not sufficiently electro-positive to support a stable formate, although $Me_3Si(HCOO)$ might exist.

Exchange reactions such as that between $EtGe(C_2H_5COO)_3$ and Ph_2SiCl_2 , which furnishes $EtGeCl_3$, indicate surprisingly mobile RCOO groups; such exchanges occur among compounds of germanium, phosphorus and silicon, or with a carbon compound containing an activated halogen. The elements germanium, silicon and phosphorus have comparable covalent single bond radii and probably the changes in entropy are finite but small.

Dimethylgermanium diacetate and 100% sulfuric acid liberated the expected quantity of anhydrous acetic acid, but the crystalline solid product was too difficultly soluble even in nitromethane to permit purification.

All three trimethylsilicon esters boil at lower temperatures than the corresponding free acids—*n*-butyric, chloroacetic and benzoic—which are partially associated.

Experimental

Starting Materials.—Professor Eugene G. Rochow of this Laboratory kindly furnished 100 g. of pure ethylgermanium trichloride (used as such herein) and 4 g. of a dimethylgermanium dihalide (converted into oxide before use), thus making this study possible.

Lead formate and each of the silver salts were precipitated from faintly acidic aqueous solutions using sodium salts of the acids, with careful washing and drying; however, silver trifluoroacetate was made from aqueous trifluoroacetic acid and silver oxide, with cautious evaporation and drying.

Ethylgermanium Triformate.—Ethylgermanium triiodide did not react with anhydrous sodium formate, despite 10 hours reflux in benzene. In contrast, 9.5 g. of $EtGeI_3$ and 22 g. of powdered lead formate in 60 ml. of benzene gave a yellow lead salt at once, although heating did not occur spontaneously. A half-hour of reflux removed the iodine nearly completely from the solution; thereupon followed filtration and washing of the solid with benzene, next distillation of solvent. Distillation of 6.5 g. of product furnished a center fraction as in Table I.

Ethylgermanium Triacetate, Tripropionate, Tri-*n*-butyrate, Tri-*n*-valerate.—Typically, 24 g. of $Ag(C_2H_5COO)$ and 6.55 g. of $EtGeCl_3$ —an excess of 30% in silver salt—in 50 ml. of pure, dry benzene furnished a temperature rise of nearly 30°; after an hour of reflux on a steam-bath with shaking, there followed the usual filtration, with washing of silver salts, then distillation of benzene, and transfer of product to smaller equipment. Table I lists the distillation of the 9.6-g. product, a yield of 95%, under 2 mm. pressure. Ordinarily the triacetate, made from $EtGeI_3$, remained a supercooled liquid.

Dimethylgermanium Diacetate.—Two grams of $(Me_2GeO)_2$ and 3.5 g. of acetic anhydride were given 1.5 hr. of free reflux at 760 mm., and then the excess anhydride was distilled at 760 mm. Later the center fraction of the diacetate distilled at 94–95° under 25 mm., and practically no organogermanium oxide remained. This diacetate melts at 50°, but it can easily supercool 10–15° if not stirred or touched with a capillary tip. It would have proved instructive to use the silver acetate method also, if material had permitted.

Silicon Esters.—Twenty grams, an excess, of Me_3SiCl and 15 g. of $Ag(n-C_3H_7COO)$, suspended in 50 ml. of benzene reacted with warming; an hour of reflux and the usual subsequent treatment furnished a 10-g. yield of ester, or 80% of the theoretical. Table I lists the distillations of the various esters. Hydrolyzable chlorine was essentially absent from the pure monochloroacetate; some free benzoic acid that contaminated the benzoate was nearly all removed by centrifuging after several hours at room temperature. A 30% excess of silver salt was necessary for the diacetate and the bis-(trifluoroacetate), to ensure complete reaction.

Physical Properties and Analysis (see Table I).—Melting points are: ethylgermanium triformate, 13°; ethylger-

(1) 1932 Commonwealth Ave., Auburndale 66, Mass.

(2) H. H. Anderson, *THIS JOURNAL*, **72**, 2089 (1950).

(3) H. A. Schuyten, J. W. Weaver and J. D. Reid, *ibid.*, **69**, 2110 (1947).

(4) C. Pape, *Ber.*, **14**, 1875 (1881), b.p. 212–216°.

(5) H. Schmidt, C. Blohm and G. Jander, *Angew. Chem.*, **A59**, 233 (1947).

(6) E. G. Rochow, *THIS JOURNAL*, **70**, 1801 (1948).

TABLE I
 All compounds distilled at lowest pressure listed. Handling of $\text{EtGe}(\text{CH}_3\text{COO})_3$ as a supercooled liquid.

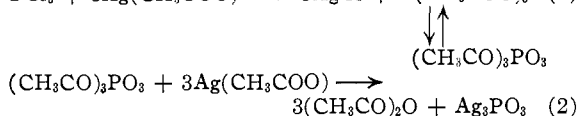
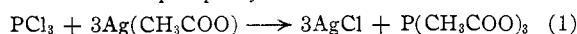
Compound	°C. B.p.	Mm.	d_{25}^{25}	n_D^{20}	R	Mol. wt.		Neut. equiv., g.	
						Calcd.	Found	Calcd.	Found
$\text{EtGe}(\text{HCOO})_3$	230 dec. 118	760 9	1.617	1.452	39.5	236.7	223	78.9	78.8, 80.1
$\text{EtGe}(\text{CH}_3\text{COO})_3$	249 99-101	760 1	1.393	1.444	53.1	278.8	320	92.9	94.0
$\text{EtGe}(\text{C}_2\text{H}_5\text{COO})_3$	256 114-116	760 2	1.271	1.4434	67.0	320.9	230*	107.0	105.3, 105.3
$\text{EtGe}(n\text{-C}_3\text{H}_7\text{COO})_3$	271 dec. 136-137	760 2	1.186	1.4432	81.2	363.0	..	121.0	119.7, 119.5
$\text{EtGe}(n\text{-C}_4\text{H}_9\text{COO})_3$	305 157-159	760 2	1.136	1.4456	95.0	405.0	..	135.0	133, 133.5
$\text{Me}_2\text{Ge}(\text{CH}_3\text{COO})_2$	188 94-95	760 25	220.8	205	110.4	109.5
$\text{Me}_3\text{Si}(n\text{-C}_3\text{H}_7\text{COO})$	144	760	0.874	1.4005	44.5	160.3	157	160.3	159.8, 159.4
$\text{Me}_3\text{Si}(\text{C}_6\text{H}_5\text{COO})$	221	760	1.004	194.3	182	194.3	192.0, 192.7
$\text{Me}_3\text{Si}(\text{CH}_2\text{ClCOO})$	159 70-71	760 30	1.057	1.4231	40.2	166.7	173	166.7	168, 165
$\text{Et}_2\text{Si}(\text{CF}_3\text{COO})_2$	155	760	1.270	312.2	306	156.1	154, 154
$(\text{C}_6\text{H}_5)_2\text{Si}(\text{CH}_3\text{COO})_2$	176-178	3	300.4	...	150.2	149

* Low probably because of decomposition.

manium triacetate, 49°, supercooling easily; diethylgermanium diacetate, 50°, also supercooling easily; trimethylbenzoxysilane, about -15°; trimethyl-(monochloroacetoxy)-silane, -20°. Diphenyldiacetoxy silane was quite viscous at 25° and completely fluid at 100°. Ethylgermanium tributrylate was more viscous than carbon tetrachloride. All were colorless, and had odors weakly suggestive of the free acid. Ethanolic sodium hydroxide solution and micro-pipets were useful in titrations of available acidity. Molecular weights used camphor for liquids boiling above 200°, or vapor densities for lower-boiling liquids.

Unsuccessful Preparations.—These show decomposition as the main limitation: EtGeCl_3 (which did not react easily with Ag_3PO_4) and the appropriate silver salt yielded a crude benzoate decomposing at the b.p. of 220° under 1 mm., and a crude monochloroacetate of b.p. 195° under 2 mm., containing excessive available acidity, neut. equiv., 108. Crude $\text{PhSi}(\text{CH}_3\text{COO})_3$ decomposed rapidly under distillation at 3 mm. Lead formate and MeSiCl_3 gave a product decomposing vigorously when heated under 25 mm. pressure; lead formate and $n\text{-Pr}_2\text{GeI}_2$ did not react.

Phosphorus trichloride and silver acetate, 7.3 g. and 39 g., respectively, in 80 ml. of benzene, reacted with much evolution of heat; after an hour of reflux and filtering, washing and removal of solvent by distillation, 4 g. of product boiled at 56-57° under 37 mm. At 760 mm. the b.p. was 140°; also, d_{25}^{25} 1.081, and n_D^{20} 1.3904. This information is consistent with data for acetic anhydride, and the reaction follows that found for phosphoryl chloride and thallose acetate.⁵



These equations are similar to the previous ones,⁵ in which the authors could have used silver acetate; phosphorus triacetate can plausibly isomerize into acetyl phosphite, which can react further with silver acetate to give acetic anhydride and silver phosphite. In this phosphorus is acidic and silver acetate is essentially basic. Other evidence, presented in the section on reactions of esters, indicates that phosphorus triacetate may be a stable compound, but should be made by an exchange reaction. In contrast, silicon and germanium are less acidic than phosphorus, and their acetates are more stable to silver acetates.

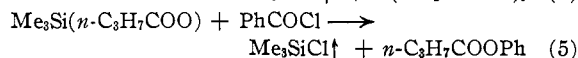
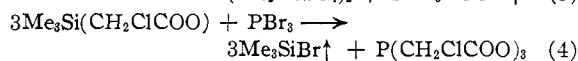
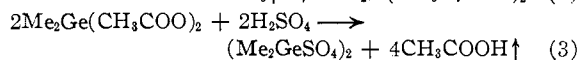
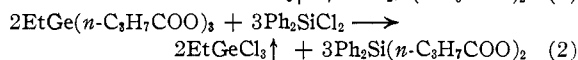
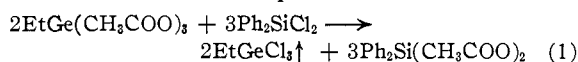
Germanium tetrachloride and acetic acid, even under 10 hours of free reflux, evolved very little hydrogen chloride, and thus germanium tetrachloride is unlike zirconium tetrachloride, which yields the tetraacetate with acetic acid on reflux.⁷

(7) A. Rosenheim and J. Hertzmann, *Ber.*, **40**, 813 (1907).

Bis-(trialkylsilicon) Sulfates by Silver Sulfate Method.

Silver sulfate converted trialkylchlorosilanes into the sulfates if nitromethane or nitrobenzene is used as solvent; this method is believed to be new. After 10 hours of reflux, 12 g. of Me_3SiCl and 24 g. of Ag_2SO_4 suspended in 20 ml. of nitromethane ultimately yielded 4.5 g. of crude $(\text{Me}_3\text{Si})_2\text{SO}_4$, after filtration and washing of the silver salts. This yield of 30% is intermediate between that obtained with a salt like $\text{Ag}(\text{CH}_3\text{COO})$ and failure to react with Ag_3PO_4 . Benzene is not a good solvent for use with silver sulfate. A yield of 60% resulted when 21 g. of Et_3SiCl and 24 g. of Ag_2SO_4 in 40 ml. of nitrobenzene were given 5 hr. reflux with occasional shaking; 12 g. of product boiled at 279° with slight decomposition, had a refractive index of 1.443 at 20°, also reacted with water when shaken to give an organosilicon layer of low density. Perhaps the best way to make a trialkylsilicon sulfate would be to treat a trialkylacetoxy silane with a slight deficiency of sulfuric acid (100%). Previously bis-(trialkylsilicon) sulfates were prepared from concentrated sulfuric acid and hexamethyldisiloxane or hexaethyl-disiloxane.⁸

Reactions of Esters.—Equations show the reactions.



Upon gentle reflux the most volatile product (designated by \uparrow) escaped; this compound was identified by boiling point, refractive index and hydrolysis products. Typically, in equation 2, 6 g. of triester and 7.8 g. of Ph_2SiCl_2 yielded 3.4 g. of EtGeCl_3 in a 20-minute reflux under 43 mm.—b.p. 95°. Other reactions were at 760 mm. In equation 4 this is probably the appropriate method for making esters of phosphorus. The most volatile product boiled (760 mm.) at 139-142°, 142°, 119°, 82-83° and 57-60° in reactions 1 to 5, respectively. Equation 3 is a transesterification, while the others are exchanges. Space does not allow a discussion of the many known exchange reactions of silanes.

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(8) L. H. Sommer, E. W. Pietrusza, G. T. Kerr and F. C. Whitmore, *This Journal*, **68**, 156 (1946); L. H. Sommer, G. T. Kerr and F. C. Whitmore, *ibid.*, **70**, 445 (1948).