NOTES

Di-*n*-propylgermanium Esters, Halides, Oxide and Sulfate

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To previously prepared alkylgermanium oxides, esters, halides and sulfates[2] there is now added di-*n*-propylgermanium oxide trimer and some derivatives. Bis-(tri-*n*-propylgermanium) oxide is converted into tri-*n*-propylgermanium fluoride, which upon bromination and subsequent hydrolysis yields a mixture of di-*n*-propylgermanium oxide and bis-(tri-*n*-propylgermanium) oxide; this procedure follows the Flood method.[3] These oxides must be converted into fluorides (or conceivably even chlorides) for easy separation by distillation; the hydrolysis of pure di-*n*-propylgermanium difluoride yields pure di-*n*-propylgermanium oxide, which oxide is trimeric according to molecular weight determinations. This trimeric oxide melts at 5.8°, but upon standing changes into a form melting at 153°—which when melted reverts to the form melting at 5.8°. Thus the new oxide resembles diethylgermanium oxide.

This method of preparing di-*n*-propylgermanium oxide is tedious, but avoids any possible rearrangement of propyl into isopropyl groups.

Di-*n*-propylgermanium oxide nearly quantitatively furnishes di-*n*-propylgermanium dichloride, dibromide and diiodide with concentrated halogen acid, or furnishes the diacetate with acetic anhydride. Transesterification of the diacetate with monochloroacetic acid gives di-*n*-propylgermanium bis-(monochloroacetate), while transesterification of the monochloroacetate with a slight deficiency of 100% sulfuric acid gives dimeric di-*n*-propylgermanium sulfate.

In transesterifications the less volatile acid displaces the more volatile acid apparently without regard for dissociation constants[2,4] which are so important in esterifications; in preparing an organogermanium sulfate by transesterification rather than by esterification water is not a product and cannot hydrolyze the sulfate.

Experimental

Table I presents the numerical data.

Di-*n*-propylgermanium Difluoride.—Tri-*n*-propylgermanium fluoride, b.p. 203°, was prepared from 40 g. of bis-(tri-*n*-propylgermanium) oxide and excess 48% hydrofluoric acid in a transparent plastic container; after extraction of the fluoride with (30–60°) petroleum ether and evaporation of the solvent, the fluoride was treated with 0.5 g. of iron powder and 33 g. of bromine, added stepwise, with reflux for six hours on a steam-bath. Following hydrolysis with alkali, then extraction with petroleum ether, 29 g. of oxides inseparable by distillation resulted. However, when converted into fluorides and then distilled under 760 mm. pressure, 10.2 g. of di-*n*-propylgermanium difluoride boiled at 182° and 8.8 g. of tri-*n*-propylgermanium fluoride boiled at 201°.

Thirty grams of tri-*n*-propylgermanium fluoride and 10 g. of iodine did not react at the boiling point of the mixture, even in the presence of aluminum iodide. This mixture, plus 0.3 g. of iron powder and 24 g. of bromine, was heated 16 hours on the steam-bath; after alkaline hydrolysis, the resultant oxides were converted into fluorides, yielding 13 g. of di-*n*-propylgermanium difluoride and 4 g. of tri-*n*-propylgermanium fluoride.

Distillation of 19 g. of 80% pure di-*n*-propylgermanium difluoride in a total-reflux, variable-takeoff column, 50 cm. long and 8 mm. i.d., filled with stainless steel helices yielded 1.9 g. boiling at 181–182°, 7.5 g. of pure difluoride at 181.8–182.1°, 3.9 g. at 182.1–182.8°, 1.6 g. at 183–191° and 3.8 g. higher boiling; all temperatures are uncorrected, at 764 mm. pressure.

Table I

Properties of New Di-*n*-propylgermanium Derivatives

Compound[a]	B.p., °C.	M.p., °C.	d^{20}_4	n^{20}	Mol. wt. (camphor) Calcd.	Found	Halogen or ester, % Calcd.	Found	Distilled at °C.	Mm.
$(n\text{-}Pr_2GeO)_3$	320	5.8	1.240	1.473$_0$	524	500	(41.5	40.8% Ge)	148–149	1
$n\text{-}Pr_2GeF_2$	182.8	0.5	1.248	1.412$_8$	196.8	204	19.3	19.3, 19.2	181.8–182.1	764[b]
$n\text{-}Pr_2GeCl_2$	209.5	−45.0	1.275	1.472$_5$	229.7	222	30.9	31.1, 31.0	209.4–210.2	777
$n\text{-}Pr_2GeBr_2$	240.5	−52.0	1.689	1.517$_3$	318.5	324	50.2	50.2, 50.2	111.8–112.3	12
$n\text{-}Pr_2GeI_2$	276.5	−53.5	2.024	....	412.6	400	61.5	61.3, 61.5	128.2–128.6	9
$n\text{-}Pr_2Ge(CH_3COO)_2$	244.6	35.6	...	....	276.8	260	42.6	42.2	89	1
$n\text{-}Pr_2Ge(CH_2ClCOO)_2$	296 dec.	....	1.374	1.479$_3$	345.8	260	54.1	54.4	143–145	2
$(n\text{-}Pr_2GeSO_4)_2$	.....	129	...	....	509.7	470	37.7	37.4		

[a] All compounds are colorless. Molar refractions in white light, oxide to bromide, 39.6, 39.3, 50.5, 57.1 ml., respectively (n^2 formula); monochloroacetate, 71.1. [b] B.p. of fluoride at 764 mm. is uncorrected.

Trimeric Di-*n*-propylgermanium Oxide.—Hydrolysis of 8.5 g. of the pure difluoride with 30 g. of 20% aqueous sodium hydroxide and then extraction of the solution with carbon tetrachloride, followed by evaporation of the solvent, gave 7.4 g. of a colorless liquid oxide distilling at 148–149° under 1 mm. pressure. Trimeric, the oxide melts at 5.8°, but slowly changes into another form melting at about 153°; in melting the 153° form reverts to the form melting at 5.8°.

Di-*n*-propylgermanium Dichloride and Dibromide.—In each case a mixture of 5.6 g. of di-*n*-propylgermanium oxide and 23 g. of concentrated halogen acid was heated to boiling, then cooled for two hours and extracted with petroleum ether. After distilling the solvent, approximately 0.2 g. of the oxide was added to react with free hydrogen halide, and the product distilled, with a quantitative yield.

Di-*n*-propylgermanium Diiodide.—A mixture of 5.6 g. of the oxide and 33 g. of freshly-prepared 48% hydriodic acid was shaken thoroughly at 70°, let stand overnight and extracted with petroleum ether. Dried over sodium sulfate, the solution finally gave a 96% yield of the diiodide after removal of solvent.

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[1] 1932 Commonwealth Ave., Auburndale 66, Mass.

[2] H. H. Anderson, This Journal, **71**, 1799 (1949); **72**, 194, 2089 (1950); **73**, 5439, 5440 (1951).

[3] E. A. Flood, *ibid.*, **54**, 1665 (1932).

[4] H. H. Anderson, *ibid.*, **73**, 5798 (1951).

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 $(R_2GeO)_{3\text{ or }4}$ 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%, this[3] method is less desirable for precious germanium compounds than the use of silver, lead or thallous salts, which are more covalent than the corresponding sodium salts. Tri-*n*-propylbromosilane and silver acetate yielded tri-*n*-propylacetoxysilane,[4] while thallous acetate[5] 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. Solvolysis[5] 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; previously[2] 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 electropositive 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 $(Me_2GeO)_4$[6] 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 $Ag(n\text{-}C_3H_7COO)$, 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-(trifluoracetate), to ensure complete reaction.

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

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[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).