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Triethylgermanium Mercaptides and Benzoates

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Table I lists the properties of ten new triethylgermanium mercaptides and two triethylgermanium benzoates. Mercaptans less volatile than acetic acid furnish triethylgermanium mercaptides through removal of acetic acid by fractional distillation, typically $(C_2H_5)_3GeOCOCH_3 + HSC_6H_5 \rightarrow (C_2H_5)_3GeSC_6H_5 + CH_3COOH \uparrow$. A reaction between $[(C_2H_5)_3Ge]_2O$ and C_6H_5SH produces $(C_2H_5)_3GeSC_6H_5$ easily, but $[(C_2H_5)_3Ge]_2O$ and C_2H_5SH yield practically no $(C_2H_5)_3GeSC_2H_5$.

TABLE I

PROPERTIES OF MERCAPTIDES AND BENZOATES

Compound	B.P.,[a] °C	MM.	d_4^{20}	n^{20}	Mol. wt.		S or OCOR		Germanium	
					Calc'd	Found	Calc'd	Found	Calc'd	Found
$(C_2H_5)_3GeSC_6H_5$	286 112–113	760 1	1.153	1.553	268.9	271	11.9	12.0	27.0	27.2
$(C_2H_5)_3Ge$-*o*-$SC_6H_4CH_3$	298 123–124	760 1	1.141	1.553	283.0	293	11.3	11.2	25.6	25.9
$(C_2H_5)_3Ge$-*m*-$SC_6H_4CH_3$	300 143–145	760 1	1.131	1.550	283.0	286	11.3	11.3	25.6	25.4
$(C_2H_5)_3GeSCH_2C_6H_5$	305 130–131	760 1	1.139	1.549	283.0	290	11.3	11.3	25.6	25.4
$(C_2H_5)_3Ge$-*o*-$SC_6H_4NH_2$[b]	326 163–164	760 1	1.197	1.583	284.0	276	11.3	11.3	25.5	25.1
$(C_2H_5)_3Ge$-β-$SC_{10}H_7$	367[c] 195–197	760 1	1.184	1.613	319.0	313	10.0	10.0	22.7	22.4
$(C_2H_5)_3GeSCH_2OC_4H_3$[b]	276[c] 130–132	760 1	1.177	1.522	272.9	284	11.7	11.7	26.6	26.5
$(C_2H_5)_3GeS$-*n*-C_6H_{13}	277 108–109	760 1	1.029	1.488	277.0	273	11.6	11.5	26.2	26.0
$(C_2H_5)_3GeS$-*n*-C_7H_{15}	288 117–118	760 1	1.019	1.489	291.0	302	11.0	10.9	24.9	24.8
$(C_2H_5)_3GeS$-*n*-$C_{12}H_{25}$	357 184–186	760 1	0.975	1.481	361.2	348	8.9	8.6	20.1	19.8
$(C_2H_5)_3GeOCOC_6H_5$[d]	290 105–107	760 1	1.172	1.513	280.9	268	43.1	43.3	25.8	—
$(C_2H_5)_3Ge$-*o*-$OCOC_6H_4NH_2$	331 174–176	760 1	1.215	1.544	295.9	310	45.8	46.4	24.5	24.4

[a] Distillation of each compound at the lowest pressure listed. [b] Pale yellow liquid. [c] Slight decomposition. [d] Center fraction.

Prior publications have listed $(C_2H_5)_3GeSCH_2COOGe(C_2H_5)_3$ as the only compound[1] containing both ethyl groups and the Ge—S mercaptide linkage, but have contained many unsubstituted mercaptides such as $(C_2H_5S)_4Ge$.[2] Recent papers from this institute reported numerous triethyltin mercaptides such as $(C_2H_5)_3SnSC_2H_5$[3] and $(C_2H_5)_3SnSCH_3$.[4]

This present paper shows the properties of ten previously unreported triethylgermanium mercaptides, all derived from mercaptans which have boiling points higher than that of acetic acid, 118°. This paper includes preparative methods, and contains information on the reactions of triethylgermanium mercaptides. There are also two previously unreported compounds $(C_2H_5)_3GeOCOC_6H_5$ and $(C_2H_5)_3Ge$-*o*-$OCOC_6H_4NH_2$.

In the reaction of $(C_2H_5)_3GeOCOCH_3$ and *meta*-$CH_3C_6H_4SH$ 93% of the products is a mixture of $(C_2H_5)_3Ge$-*m*-$SC_6H_4CH_3$ and CH_3COOH, while an indicated 7% is a mixture of $(C_2H_5)_3Ge$-*m*-$OC_6H_4CH_3$ and CH_3COSH. Moreover, $(C_2H_5)_3GeOCOCH_3$ and *ortho*-$NH_2C_6H_4SH$ react to yield 90% of mixed $(C_2H_5)_3Ge$-*o*-$SC_6H_4NH_2$ and CH_3COOH, while an indicated 10% is a mixture of $(C_2H_5)_3Ge$-*o*-$OC_6H_4NH_2$ and CH_3COSH, according to the following evidence. First, the acetic acid fraction boiled at only 113°, had a weak odor of CH_3COSH, and was not completely miscible with water. Second, the small fraction supposedly $(C_2H_5)_3Ge$-*o*-$OC_6H_4NH_2$ was colorless and boiled 30° lower, under 1 mm. pressure, than the pale-yellow $(C_2H_5)_3Ge$-*o*-$SC_6H_4NH_2$. Third, the fractional distillation required very careful collection of the highest-boiling fraction, to yield a product containing the calcu-

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(1) Anderson, *J. Am. Chem. Soc.*, **72**, 2089 (1950).

(2) Backer and Stienstra, *Rec. trav. chim.*, **52**, 1033 (1933); **54**, 38, 607 (1935).

(3) Sasin, *J. Org. Chem.*, **18**, 1142 (1953).

(4) Anderson and Vasta, *J. Org. Chem.*, **19**, 1300 (1954).

lated amount of mercaptide sulfur, rather than a low amount; this precaution in fractional distillation was typical throughout the present paper. Boiling points are unfavorable for reactions between $(C_2H_5)_3GeOCOCH_3$ and either n-C_4H_9SH or n-$C_5H_{11}SH$, which depend upon removal of CH_3COOH by fractional distillation.

It is not advisable to prepare $(C_2H_5)_3GeS$-n-C_4H_9 or $(C_2H_5)_3GeS$-n-C_5H_{11} from $[(C_2H_5)_3Ge]_2O$, b.p. 254°,[5] because the boiling points could be too close together for good separation by fractional distillation. Under reflux conditions $[(C_2H_5)_3Ge]_2O$ reacts extremely slowly with C_2H_5SH. However, reaction of $[(C_2H_5)_3Ge]_2O$ and C_6H_5SH, a higher-boiling mercaptan of comparatively greater acidity than that of C_2H_5SH, yields $(C_2H_5)_3GeSC_6H_5$ and water easily.

Pure triethylgermanium mercaptides seem to react slowly with higher-boiling mercaptans, with weak organic acids such as benzoic acid, or with $(C_6H_5)_2SiCl_2$. The reaction between $(C_2H_5)_3GeSC_6H_5$ and 2-naphthalenethiol yields $(C_2H_5)_3Ge$-β-$SC_{10}H_7$ and C_6H_5SH, as expected, but separation by fractional distillation is comparatively difficult.

Briefly, the preparation of triethylgermanium mercaptides is more intricate than preparations of analogous triethyltin mercaptides; any method yielding $(C_2H_5)_3GeSC_2H_5$ apparently must be novel.

EXPERIMENTAL

Starting materials. These included the following: pure $(C_2H_5)_3GeBr$[5] and $(C_2H_5)_3GeOCOCH_3$[1] made from pure $[(C_2H_5)_3Ge]_2O$[1,5] and acetic anhydride or hydrobromic acid; Eastman Kodak white label mercaptans, and furfuryl mercaptan from Aldrich Chemical Co., Milwaukee 12, Wisconsin.

Analytical methods. These included the following: conversion of the individual compound to GeO_2 in a Vycor crucible with cover, using fuming nitric and sulfuric acids; titration of mercaptide sulfur with KI_3 solution (difficult with the amino derivative); titration of benzoic and *ortho*-aminobenzoic acids with sodium hydroxide in ethanol; molecular weights by the lowered freezing point of a camphor solution.

Equipment. Distilling equipment consisted of interchangeable units with ground joints; the distilling column was a 25-cm. length of unpacked tubing 3 mm. in i.d., rating at least 6 plates in slow distillation with a high reflux ratio.

Reactions of $(C_2H_5)_3GeOCOCH_3$. Reaction of 12 millimoles of $(C_2H_5)_3GeOCOCH_3$ and 10.5 millimoles of *ortho*-$CH_3C_6H_4SH$ yielded 10 millimoles of acetic acid in 15 minutes of gentle reflux; fractional distillation, first under 20 mm. and finally under 1 mm. pressure, yielded 9.7 millimoles (2.74 g.) of $(C_2H_5)_3Ge$-o-$SC_6H_4CH_3$, the highest-boiling 1.7 g. of which served for study of properties. Similarly, other reactions gave yields of approximately 90% based on available mercaptan; reflux periods were 10–15 minutes with the HSC_6H_4-type, or 2-naphthalenethiol, or *ortho*-aminobenzoic acid, and 40–65 minutes with other mercaptans.

Triethylgermanium benzoate. A 30-minute reflux of 12 millimoles of $(C_2H_5)_3GeBr$ and 16 millimoles of silver benzoate in 10 ml. of CCl_4[6] furnished 11 millimoles of $(C_2H_5)_3GeOCOC_6H_5$, a yield of 90%.

Reaction of $[(C_2H_5)_3Ge]_2O$ and mercaptans. Five millimoles of the organogermanium oxide and 14 millimoles of C_6H_5SH reacted even at 25°; after 10 minutes at 100° there followed cooling, centrifuging, separation from the water layer, drying with Na_2SO_4, then fractional distillation. A yield of 6.7 millimoles of $(C_2H_5)_3GeSC_6H_5$ resulted, the highest-boiling 60% of which had the following properties: b.p. 289°; d_4^{20} 1.153; n^{20} 1.549; S, 11.8. Yet the organogermanium oxide and C_2H_5SH reacted extremely slowly under reflux according to the b.p. and mercaptide content.

Reactions of organogermanium mercaptides. Reflux of 6 millimoles of $(C_2H_5)_3GeSC_6H_5$ and 5 millimoles of *beta*-$C_{10}H_7SH$ under 20 mm. pressure for 30 minutes furnished 5 millimoles of $(C_2H_3)_3Ge$-β-$SC_{10}H_7$, b.p. 365°, and 5 millimoles of C_6H_5SH, but the separation by fractional distillation was difficult. Reflux of $(C_2H_5)_3GeSCH_2OC_4H_3$ and a deficiency of benzoic acid under the same conditions gave only a partial reaction. A short reflux of $(C_2H_5)_3Ge$-β-$SC_{10}H_7$ with $(C_6H_5)_2SiCl_2$, with fractional distillation, produced a 25% yield of $(C_2H_5)_3GeCl$, b.p. 171°.[5]

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(5) Kraus and Flood, *J. Am. Chem. Soc.*, **54**, 1635 (1932).

(6) Anderson, *J. Am. Chem. Soc.*, **74**, 2371 (1952).