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PREPARATION AND THERMAL REACTIONS OF SOME TRIMETHYLMETAL DERIVATIVES OF DIFUNCTIONAL ORGANIC REAGENTS

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SUMMARY

The trialkyltin derivatives of difunctional organic reagents such as thioglycol, glycolic acid, thioglycolic acid and so on and the trimethylmetal (M = Si, Ge, Sn) derivatives of thioglycol were prepared, and their thermal properties were investigated. A novel disproportionation reaction was found for some trimethyltin derivatives, which gave tetramethyltin and dimethyltin derivatives. Bis(trimethyltin) thioglycolate was the least stable, and decomposed even at room temperature.

INTRODUCTION

It has been reported in a few cases that some triorganotin derivatives decompose into tetraorganotin and/or diorganotin derivatives at relatively low temperatures. One case was reported by van der Kerk *et al.*[1] during the studies on decarboxylation reactions of organotin carboxylates. Bis(triphenyltin) malonate and trialkyltin ethyl malonates decompose on heating giving tetraorganotin as the main product. In our laboratory trimethyltin oxinate was found to partly decompose during the distillation process giving dimethyltin dioxinate[2]. Quite recently it was also found that bis(trialkyltin) glycoxides or thioglycoxides decompose on heating into tetraalkyltin and dialkyltin glycoxide or thioglycoxide[3].

The series of trialkylmetal derivatives described in this paper were prepared in order to investigate the possibility of such disproportionation reactions with trialkyl substituted metal derivatives.

EXPERIMENTAL

$R_3SnSCH_2CH_2OH$ [$R = CH_3$ (*I*), n-C_4H_9 (*I'*)]

To a solution of equimolar amounts of trimethyltin chloride and thioglycol in benzene was added an equimolar amount of triethylamine. The precipitate of triethylamine hydrochloride was filtered off, and the solvent was removed under reduced pressure. By a vacuum distillation of the residual liquid, (I) was obtained in a yield of 53% and a small amount of $(CH_3)_2Sn(SCH_2CH_2O)$ remained. IR for (I) (neat): ν(O–H) 3410 s(br), ν(Sn–S) 342 m cm^{-1}.

(I') was obtained in a similar manner. IR (neat): ν(O–H) 3400 s(br), ν(Sn–S) 337 s cm^{-1}.

$R_3SnOOCCH_2OH$ [$R = CH_3$ (II), n-C_4H_9 (II')]

To a solution of trimethyltin methoxide, prepared by the reaction of trimethyltin chloride (5.42 g, 0.027 mole) and sodium (0.62 g, 0.027 mole) in methanol (50 ml), was added a solution of glycolic acid (2.30 g, 0.030 mole) in methanol (10 ml). The mixture was concentrated to a half amount under reduced pressure, and n-hexane (20 ml) was added, from which the crystals of (II) (2.50 g) were obtained in pure form by fractional crystallization. IR (Nujol): ν(O–H) 3430, 3365 s, ν_a(CO_2) 1573 vs cm^{-1}.

A solution of hexa-n-butyldistannoxane (16.4 g, 0.0273 mole) and glycolic acid (4.60 g, excess) in toluene (200 ml) was refluxed for 2 h and concentrated to a half amount. Addition of n-hexane to the solution gave crystals of (II') (11.7 g), which were recrystallized from n-hexane. IR (Nujol): ν(O–H): 3175 m(br), ν_a(CO_2) 1626 vs cm^{-1}.

$(CH_3)_3SnS(CH_2)_nCOOSn(CH_3)_3$ [$n = 1$ (III), 2 (IV)]

To an ice-cold solution of trimethyltin chloride (4.0 g, 0.020 mole) in water (100 ml), which was previously deaerated by bubbling nitrogen through it, was added thioglycolic acid (0.92 g, 0.010 mole) under nitrogen atmosphere and then triethylamine (2.5 g, excess). The resulting white precipitate was filtered, washed with water, dried in air (yield, 2.7 g). and recrystallized quickly from n-hexane. IR (Nujol): ν_a(CO_2) 1588, 1570 vs, ν_s(CO_2) 1435 s cm^{-1}. IR ($CHCl_3$): ν_a(CO_2) 1644 s, ν_s(CO_2) 1330 s cm^{-1}.

(IV) was prepared in a similar manner from trimethyltin chloride and 3-mercaptopropionic acid in water. IR (Nujol): ν_a(CO_2) 1566 cm^{-1}.

$(CH_3)_3SnOOCCOOSn(CH_3)_3 \cdot 2\,H_2O$ (V) and its anhydrous homologue (V')

To a solution of trimethyltin chloride (5.77 g, 0.0288 mole) and oxalic acid dihydrate (1.81 g, 0.0144 mole) in water (50 ml) was added, with stirring, triethylamine (3.28 g, excess). The resulting white precipitate was filtered, washed with water, dried in air (yield 4.16 g). Its elemental analysis agreed well with (V). IR (Nujol): ν(O–H) 3230 s(br), δ(OH_2) or ν_a(CO_2) 1600 vs cm^{-1}.

The dihydrate was heated at 125° for 5 h during which water was separated. The elemental analysis of the residual solid agreed well with (V'). IR (Nujol): ν_a(CO)$_2$ 1602 vs cm^{-1}. This compound has been recently prepared by the reaction of tetramethyltin and mercury(I) oxalate[4].

$(CH_3)_3GeSCH_2CH_2OH$ (VI) and $(CH_3)_3GeSCH_2CH_2OGe(CH_3)_3$ (VII)

To a solution of trimethylchlorogermane (1.535 g, 0.0100 mole) and thioglycol (0.786 g, 0.0100 mole) in dry benzene (20 ml) was added triethylamine (1.06 g, 0.0105 mole) with stirring. The precipitate of triethylamine hydrochloride was filtered off, and the solvent was removed under reduced pressure. The elemental analysis of the residual liquid (1.6 g) agreed well with (VI). IR (neat): ν(O–H) 3390 s(br), ν(Ge–S) 379 m cm^{-1}. Distillation under reduced pressure of this product gave 70% yield of colorless liquid (b.p. 78–111°/18 mmHg). Examination of the IR and PMR spectra of the fractional distillates showed that some disproportionation had occurred: thioglycol mixed in the early stage and (VII) in the later.

The pure compound (VII) was prepared in the same manner as (VI) using trimethylchlorogermane (4.602 g, 0.0300 mole), thioglycol (1.182 g, 0.0150 mole) and triethylamine (3.344 g, 0.0330 mole) in dry benzene (50 ml). Distillation of the resulting liquid under reduced pressure gave 2.64 g of colorless liquid (b.p. 80–84°, mainly 83–84° at 3 mmHg). The elemental analysis agreed well with (VII).

$(CH_3)_3SiOCH_2CH_2SM$ ($M=H$ (VIII), $Ge(CH_3)_3$ (IX), $Sn(CH_3)_3$ (X))

A mixture of hexamethyldisilazane (10.0 g, 0.062 mole) and thioglycol (8.6 g, 0.110 mole) was heated at 100° under a slow nitrogen stream. After 6 h, 95% of ammonia was trapped in 0.1 *N* HCl solution at the gas outlet. From the reaction mixture, (VIII) was isolated by a fractional distillation in a yield of 60%. IR (neat): ν_a(Si–O–C) 1080 cm^{-1}.

In another experiment, it was found that an excess of hexamethyldisilazane did not react with the terminal S–H group of (VIII), even after a prolonged heating.

The other two compounds, (IX) and (X), were easily prepared in the same

TABLE 1

ANALYTICAL DATA OF THE TRIALKYLMETAL DERIVATIVES

Compound	*M.p. or b.p.* [°*C*], (°*C/mmHg*)	n_D^{20}	*Analysis found (calcd.)* (%)			*Mol.wt. found (calcd.)*
			C	*H*	*Sn*	
$(CH_3)_3SnSCH_2CH_2OH$ (I)	(79–81/3.5)	1.5502	24.86 (24.93)	5.85 (5.86)		242[a] (241)
$(n\text{-}C_4H_9)_3SnSCH_2CH_2OH$ (I′)	(153/4)	1.5175	45.19 (45.80)	9.37 (8.79)		376[a] (367)
$(CH_3)_3SnOOCCH_2OH$ (II)	[121 dec.]		25.02 (25.14)	5.31 (5.06)	49.52 (49.69)	
$(n\text{-}C_4H_9)_3SnOOCCH_2OH$ (II′)	[79–80]		46.01 (46.06)	8.05 (8.28)	32.38 (32.51)	
$(CH_3)_3SnSCH_2COOSn(CH_3)_3$ (III)	[Dec.]		23.07 (23.00)	4.89 (4.83)	56.88 (56.83)	413[b] (418)
$(CH_3)_3SnSCH_2CH_2COOSn(CH_3)_3$ (IV)	[111.5–113]		24.97 (25.04)	5.01 (5.14)	54.73 (54.98)	
$(CH_3)_3SnOOCCOOSn(CH_3)_3 \cdot 2\,H_2O$ (V)	[ca. 110 dec.]		21.21 (21.28)	4.96 (4.91)	52.76 (52.56)	
$(CH_3)_3SnOOCCOOSn(CH_3)_3$ (V′)	[ca. 200 dec.]		22.89 (23.12)	4.40 (4.37)	57.41 (57.12)	
$(CH_3)_3GeSCH_2CH_2OH$ (VI)	(Dec.)	1.5097	30.76 (30.83)	7.16 (7.24)		202[a] (195)
$(CH_3)_3GeSCH_2CH_2OGe(CH_3)_3$ (VII)	(83–84/2.5)	1.4885	30.50 (30.85)	7.09 (7.12)		
$(CH_3)_3SiOCH_2CH_2SH$ (VIII)	(153–154/760)	1.4387	39.71 (39.95)	9.70 (9.39)		150[c] (150)
$(CH_3)_3GeSCH_2CH_2OSi(CH_3)_3$ (IX)	(62–65/2)	1.4668	35.97 (35.99)	8.46 (8.31)		282[a] (267)
$(CH_3)_3SnSCH_2CH_2OSi(CH_3)_3$ (X)	(81–82/3)	1.4958	30.61 (30.69)	7.28 (7.08)		319[a] (313)

[a] Cryoscopic method in benzene. [b] VPO method in $CHCl_3$. [c] Mass spectroscopy.

TABLE 2

PMR DATA OF THE TRIALKYLMETAL DERIVATIVES[a]

Compound	*τ(M–CH₃)* *(ppm)*	*τ(S–CH₂)* *(ppm)*	*τ(CH₂–O)* *(ppm)*	*τ(Y–H)*[d] *(ppm)*	*J(¹¹⁹Sn–CH₃)* *(Hz)*	*J(¹¹⁷Sn–CH₃)* *(Hz)*
$(CH_3)_3SnSCH_2CH_2OH$	9.54	7.33 (t)	6.42 (t)	5.63	58.8	57.6
$(n\text{-}C_4H_9)_3SnSCH_2CH_2OH$		7.36 (t)	6.45 (t)	5.73		
$(CH_3)_3SnSCH_2COOSn(CH_3)_3$[b]	9.49	6.71			58.2	55.8
$(CH_3)_3SnSCH_2CH_2COOSn(CH_3)_3$[c]	9.53	7.05–7.80 (m)[e]			58.2	55.5
$(CH_3)_3GeSCH_2CH_2OH$	9.50	7.43 (t)	6.45 (t)	5.45		
$(CH_3)_3GeSCH_2CH_2OGe(CH_3)_3$	9.68 9.56	7.53 (t)	6.49 (t)			
$(CH_3)_3SiOCH_2CH_2SH$	9.87	7.42 (m)	6.39 (t)	8.68 (t)		
$(CH_3)_3GeSCH_2CH_2OSi(CH_3)_3$	9.91 9.53	7.44 (t)	6.38 (t)			
$(CH_3)_3SnSCH_2CH_2OSi(CH_3)_3$	9.91 9.60	7.43 (t)	6.43 (t)		56.3	53.3

[a] Measured in a pure state unless stated otherwise. [b] In chloroform (8%). [c] In dichloromethane (8%). [d] Y = oxygen or sulfur. [e] $\tau(SCH_2CH_2COO)$.

manner as above using (VI) or (I) instead of thioglycol; the yields were 88 and 68%, respectively.

The results of elemental analysis of these trialkylmetal derivatives are summarized in Table 1, and the data for the PMR spectra of the soluble compounds are shown in Table 2.

Thermal reactions of trialkylmetal derivatives

In general, the thermal reaction of trialkylmetal derivatives was carried out in a Claisen flask kept at a constant temperature on a well stirred oil bath. The distillate, when obtained, was identified by refractive index and IR spectrum. The residual material was treated with acetone or methanol, and analyzed. The analytical results are summarized in Table 3.

TABLE 3

ANALYTICAL DATA OF THE DIALKYLTIN DERIVATIVES

Compound	*M.p. (°C) (reported)*	*Analysis, found (calcd.) (%)*			*Mol.wt. found (calcd.)*	$\nu_a(CO_2)$[a] *(cm⁻¹)*
		C	*H*	*Sn*		
$(CH_3)_2Sn(SCH_2CH_2O)$		21.18	4.48	52.65	516[b]	
		(21.36)	(4.48)	(52.78)	(225)	
$(n\text{-}C_4H_9)_2Sn(SCH_2CH_2O)$	92–94	38.63	7.39	38.73	630[c]	
	(89–90)[3,6]	(38.87)	(7.18)	(38.41)	(309)	
$(CH_3)_2Sn(OCH_2COO)$				53.24		1590, 1600
				(53.27)		
$(CH_3)_2Sn(OH)(OOCCH_2OH)$		20.02	4.59	49.21		1593
		(19.96)	(4.19)	(49.30)		
$(CH_3)_2Sn(SCH_2COO)$	257–259	20.39	3.37	49.65		1553, 1578
	(257–259)[7]	(20.11)	(3.38)	(49.69)		
$(CH_3)_2Sn(SCH_2CH_2COO)$	215–216	23.72	4.02	46.63		1540
	(211.2)[8]	(23.75)	(3.99)	(46.93)		
$(n\text{-}C_4H_9)_2Sn(SCH_2COO)$[d]	182–184	37.25	6.53	36.73	2500–8000	1546, 1573
	(184.5)[8]	(37.18)	(6.24)	(36.79)	(323)	

[a] Nujol mull. [b] VPO method in pyridine. [c] Cryoscopic method in benzene. [d] Prepared by the reaction of di-n-butyltin oxide and thioglycolic acid in benzene; mol.wt. measured by VPO method in benzene at concentrations, $w/w = 0.001–0.03$ g/g; $\nu_a(CO_2)$ of 1% benzene soln. observed at 1546 cm⁻¹.

Spectra

The IR spectra in the 4000–400 cm⁻¹ region were recorded on Hitachi EPI-2G and 225 spectrophotometers equipped with gratings, and those in the region of 700–200 cm⁻¹, on a Hitachi EPI-L spectrophotometer with gratings. A Japan Electron Optics JNM-3H-60 spectrometer was used to record PMR spectra. Chemical shifts are expressed in τ values using TMS (τ 10) or cyclohexane (τ 8.56) as standard. Mass spectra were measured on a Hitachi Mass Spectrometer Model RMU-6E at 70 eV.

RESULTS AND DISCUSSION

The IR and PMR spectra of mono-substituted trialkyltin thioglycoxides (I) and (I') show that the tin atoms are bound to the sulfur atom. In the IR spectrum of trimethyltin glycolate (II), the asymmetric stretching vibration band due to the carboxyl group can be observed at 1573 cm^{-1}, which is characteristic of a symmetrical (possibly bridging) carboxylate group[5]. With thioglycolic acid, we tried several methods in order to obtain the mono-substituted trimethyltin thioglycolate, but only bis(trimethyltin) thioglycolate (III) could be isolated. This compound is monomeric in solutions of CH_2Cl_2 or $CHCl_3$, and the IR spectra show the band due to the asymmetric stretching vibration of the carboxyl group at 1644 cm^{-1} in solution and at ca. 1580 cm^{-1} in the solid state, again indicating a possible bridging structure in the solid state. An analogous bridging structure may be expected for 3-mercaptopropionate (IV).

These trimethyltin derivatives [(I)–(IV)] all decompose giving tetramethyltin when heated at ca. 110–130°. In our experiments, compound (I) was the least reactive, and the corresponding tri-n-butyltin derivative (I') also decomposed in the same manner as (I). The crystals of (II) remained transparent below 120°, but decomposed almost instantaneously when heated at 125°, giving tetramethyltin and sticky solids, from which dimethyltin glycolate was isolated. This substance was easily hydrolyzed to dimethyltin hydroxide glycolate when treated with hot methanol. Tri-n-butyltin glycolate (II') was less reactive; after ten hours of heating at 125°, a still considerable amount of the compound was recovered and only a trace of tetra-n-butyltin was

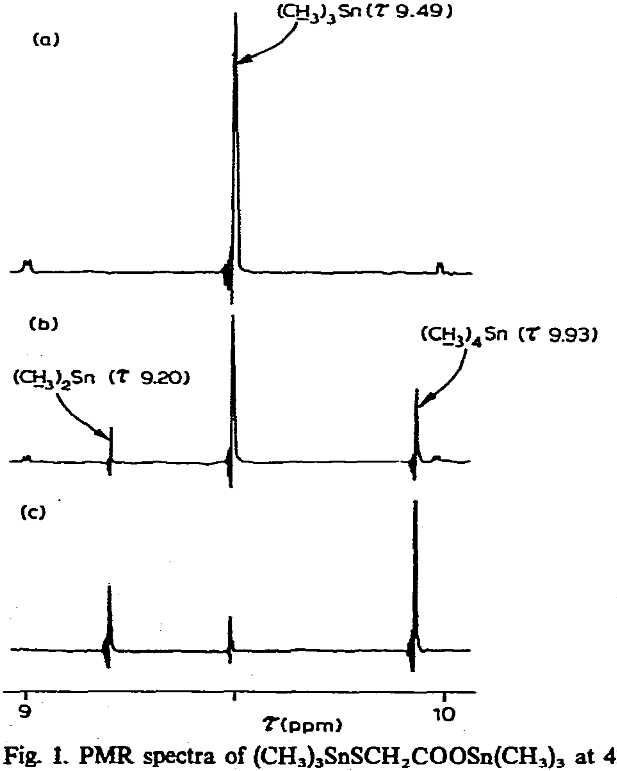

Fig. 1. PMR spectra of $(CH_3)_3SnSCH_2COOSn(CH_3)_3$ at 42° in 8% $CHCl_3$ solution. (a) After 9 min; (b) after 55 min; (c) after 115 min.

isolated. Compound (III) was the most reactive, and decomposed slowly even at room temperature. In the solid state, the reaction at room temperature was almost complete in about four months, as detected by means of IR spectra. In solution, the reaction was much faster as can be observed in the time-dependent PMR spectral change (see Fig. 1). At room temperature, the proton peaks of the trimethyltin group completely disappeared in one day. When a donor solvent like pyridine was used, the rate of spectral change was much slower. The compound (IV) was stable for weeks in solution at room temperature, but decomposed at 130° giving tetramethyltin and dimethyltin 3-mercaptopropionate.

The other compounds [(V)–(X)], on the other hand, decomposed differently or were stable even at 170°. Bis(trimethyltin) oxalate dihydrate (V) was found to dehydrate at 125°, but the anhydrous oxalate (V′) was stable even at 170°. The germanium analogue (VI) of (I) partly decomposed in a different way on distillation; thioglycol was distilled off first, then thioglycoxy-*O,S*-bis(trimethylgermyl) (VII) was obtained. The four thioglycoxides (VII)–(X) were stable at 170° and could be distilled without any reaction.

The reactions observed in the present study are summarized in the following equations:

$$\underset{\text{(I)}}{2\,(\mathrm{CH_3})_3\mathrm{SnSCH_2CH_2OH}} \xrightarrow[10\ \mathrm{h}]{125^\circ}$$

$$\mathrm{HSCH_2CH_2OH} + \underset{(42\%)}{(\mathrm{CH_3})_4\mathrm{Sn}} + \underset{(43\%)}{(\mathrm{CH_3})_2\mathrm{Sn(SCH_2CH_2O)}} \qquad (1)$$

$$\underset{\text{(II)}}{2\,(\mathrm{CH_3})_3\mathrm{SnOOCCH_2OH}} \xrightarrow[0.5\ \mathrm{h}]{125^\circ}$$

$$\begin{array}{lr} \mathrm{HOCH_2COOH} + \underset{(69\%)}{(\mathrm{CH_3})_4\mathrm{Sn}} + (\mathrm{CH_3})_2\mathrm{Sn(OCH_2COO)} & (2) \\ \qquad\qquad\qquad\qquad\qquad\qquad \big\downarrow \mathrm{H_2O} & \\ \qquad\qquad\qquad\qquad\qquad (\mathrm{CH_3})_2\mathrm{Sn(OH)(OOCCH_2OH)} & (2') \end{array}$$

$$\underset{\text{(III)}}{(\mathrm{CH_3})_3\mathrm{SnSCH_2COOSn(CH_3)_3}} \xrightarrow[1\ \mathrm{h}]{110^\circ} \underset{(64\%)}{(\mathrm{CH_3})_4\mathrm{Sn}} + \underset{(99\%)}{(\mathrm{CH_3})_2\mathrm{Sn(SCH_2COO)}} \qquad (3)$$

$$\underset{\text{(IV)}}{(\mathrm{CH_3})_3\mathrm{SnSCH_2CH_2COOSn(CH_3)_3}} \xrightarrow[4\ \mathrm{h}]{130^\circ}$$

$$\underset{(64\%)}{(\mathrm{CH_3})_4\mathrm{Sn}} + \underset{(74\%)}{(\mathrm{CH_3})_2\mathrm{Sn(SCH_2CH_2COO)}} \qquad (4)$$

$$\underset{\text{(V)}}{(CH_3)_3SnOOCCOOSn(CH_3)_3\cdot 2\,H_2O} \xrightarrow[6.5\text{ h}]{125°} \underset{\text{(V')}}{(CH_3)_3SnOOCCOOSn(CH_3)_3} + \underset{(81\,\%)}{2\,H_2O} \qquad (5)$$

$$\underset{\text{(VI)}}{2\,(CH_3)_3GeSCH_2CH_2OH} \longrightarrow \underset{\text{(VII)}}{(CH_3)_3GeSCH_2CH_2OGe(CH_3)_3} + HSCH_2CH_2OH \qquad (6)$$

In the novel disproportionation reaction observed for (I)–(IV), the fifth or sixth atom from the tin atom of the starting trialkyltin derivatives is an oxygen. This seems to suggest that a five- or six-membered chelate may be a possible intermediate in such a disproportionation reaction[3], as is also suggested for the hydrolysis intermediate of esters of the type $R_3M(CH_2)_nCOOC_2H_5$[9].

The dialkyltin derivatives of thioglycol were found to be dimeric, but the molecular weights of the other compounds could not be determined because of their poor solubilities in common organic solvents. However, such poor solubilities and observations of the assymmetric stretching band due to the carboxyl group in the C_{2v} symmetry region may be accounted for by assuming polymeric structures bridged by the carboxyl group. This hypothesis seems to be supported by the study of di-n-butyltin thioglycolate $(n\text{-}C_4H_9)_2Sn(SCH_3COO)$ which was obtained by a common reaction (Table 3).

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