.01173	42.1	3.85	51.5	26.0	16.8	5.66	1.03	
.00945	33.3	3.40	48.9	26.9	19.1	5.09	0.87	
.00917	43.9	3.61	50.3	26.2	17.9	5.62	1.21	
.00868	37.1	3.62	48.2	28.6	17.4	5.87	..	
.00786	41.2	3.54	51.2	25.6	18.7	4.50	..	
.0059	40.7	3.34	49.9	27.4	18.3	4.35	..	
C_2H_6, $R = 2.43$								
0.05998	26.7	4.44	51.5	27.4	14.9	6.13	1.30	
.0161	24.1	4.22	48.1	30.1	15.5	6.26	1.27	3.0
.0534	20.7	4.22	48.3	29.8	15.2	6.75	0.97	..
.0131	26.6	3.95	47.2	29.3	16.4	7.12	0.38	3.3
.0116	28.0	3.94	48.6	27.9	17.7	5.81	1.19	..
.0105	47.7	3.94	49.5	27.6	16.8	6.16	1.06	..
.00891	42.7	3.60	48.6	26.7	18.4	6.21	0.79	..
.0076	44.7	3.72	50.7	26.0	17.2	6.11	1.03	..
.00702	44.2	3.66	48.7	27.1	17.4	6.90	0.81	1.31
.00613	34.5	3.24	48.8	28.2	16.8	6.29	0.85	..
Toluene, $R = 1.90$								
0.0152	30.6	4.41	49.4	27.0	16.3	7.18	0.60	
.0433	40.2	4.50	49.7	27.4	16.0	6.89	.23	
.0127	42.6	4.20	50.4	25.1	17.6	6.87	.52	
.0101	38.3	4.06	48.7	27.7	16.7	6.86	.22	
.0101	45.1	4.02	51.4	25.2	17.4	6.11	.67	
.0082	37.6	3.77	50.5	25.3	17.9	6.24	.45	
.00721	44.2	3.59	48.5	27.0	18.4	6.04	..	

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF CHEMISTRY AT HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

Dimethyltin Salts of Carboxylic Acids

BY ROKURO OKAWARA[1] AND EUGENE G. ROCHOW

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Reactions of dimethyltin oxide and dichloride with formic and acetic acids and their salts have been studied. Formic acid did not react with the dichloride, but $(CH_3)_2SnCl(OOCH)$ and $(CH_3)_2Sn(OOCH)_2$ were obtained by the action of sodium formate. Acetic acid and the dichloride gave $(CH_3)_2SnCl(OOCCH_3)$ in poor yield; this compound was obtained in better yield by using acetic anhydride. Dimethyltin diacetate could not be obtained, but the dimeric compound, tetramethyl-1,3-diacetoxydistannoxane, was obtained from the oxide and acetic anhydride. Dimethylchloroformoxytin and dimethylchloroacetoxytin gave tetramethyl-1,3-dichlorodistannoxane by hydrolysis. The reverse reaction could be carried out by cleaving the dichlorodistannoxane with formic or acetic acid. Infrared spectra showed the presence of carboxylate ions in the solid state.

Various methods have been applied to the preparation of organotin esters.[2a] Van der Kerk and Luitjen[3] described trimethyltin acetate, obtained from acetic acid and trimethyltin hydroxide. Halogenoacetates of dimethyltin were prepared by the acid cleavage of dimethyldivinyltin,[2b] and some esters were obtained by the reaction of dimethyltin dichloride with alkali metal salts in aqueous solution.[4] Of the esters of the monomethyltin group, linear and cyclic tristannoxanes were obtained from the reaction of methylstannoic acid and carboxylic acids.[5]

Dimethyltin dichloride is readily available,[6] and it was thought to be interesting to attempt the preparation of esters directly from the dichloride.[7] To this end, dimethyltin dichloride was allowed to react with formic and acetic acids or their anhydrides or sodium salts. The reaction of an excess of acetic anhydride gave dimethylchloroacetoxystannane. By the reaction of glacial acetic acid, a small amount of dimethylchloroacetoxystannane was also obtained. Experiments to obtain dimethyldiacetoxystannane from chlorides or from dimethyltin oxide were carried out, but it was impossible to isolate this compound because of decomposition in the course of sublimation or because of polymerization during recrystallization. The only well-characterized product was the dimeric one, tetramethyl-1,3-diacetoxydistannoxane, $(CH_3COO)(CH_3)_2Sn{-}O{-}Sn(CH_3)_2(OOCCH_3)$, which was obtained by recrystallization. A compound having the similar distannoxane structure has been reported recently.[8] These results suggest why Lambourne[5] has obtained compounds having cyclic and linear tristannoxane structures.

While formic acid and dimethyltin dichloride showed no reaction, addition of an insufficient amount of sodium formate to the dichloride gave the chloroformoxystannane; addition of an excess amount of sodium formate gave dimethyldiformoxystannane. These compounds were also derived from polymeric dimethyltin oxide as demonstrated in the reaction scheme shown below.

This reaction scheme is also applicable in principle to the case of acetoxy compounds with slight changes; dimethylchloroacetoxystannane can be obtained by the action of acetic anhydride on the dichloride, and the position of dimethyldiacetoxystannane in this reaction scheme should be substituted by tetramethyl-1,3-diacetoxydistannoxane.

For the compounds investigated here, differences between the behavior of the Sn–Cl bond from that of the Si–Cl bond during hydrolysis are clearly shown in this scheme. In an alkaline medium, the Sn–Cl bond hydrolyzes completely to form an Sn–O–Sn linkage, but it does not react in a neutral or acidic medium.[4,9] Another difference is shown in the infrared spectra[10] of carboxylates of these two ele-

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[1] Research Fellow in Chemistry at Harvard University, 1958–1959.

[2] (a) See references 4–8 of (2b). (b) A. Saitow, E. G. Rochow and D. Seyferth, *J. Org. Chem.*, **23**, 116 (1958).

[3] G. J. M. van der Kerk and J. G. A. Luitjen, *J. Appl. Chem.*, **6**, 49 (1956).

[4] E. G. Rochow, D. Seyferth and A. C. Smith, Jr., THIS JOURNAL, **75**, 3099 (1953).

[5] H. Lambourne, *J. Chem. Soc.*, **121**, 2533 (1922); **125**, 2013 (1924).

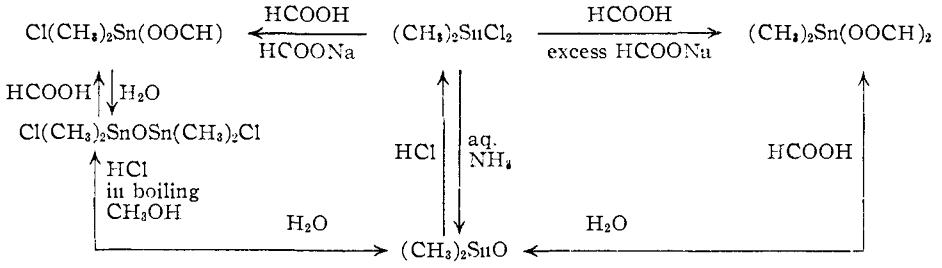
[6] A. C. Smith, Jr., and E. G. Rochow, THIS JOURNAL, **75**, 4103, 4105 (1953).

[7] The experiment to obtain triorganotin acetate directly from the reaction of triorganotin bromide and sodium acetate has not been successful. See ref. 8.

[8] S. D. Rosenberg, E. Debreczeni and E. T. Weinberg, THIS JOURNAL, **81**, 972 (1959).

[9] E. G. Rochow and D. Seyferth, *ibid.*, **75**, 2877 (1953).

[10] See also R. Okawara, D. E. Webster and E. G. Rochow, *ibid.*, **82**, 3287 (1960).



ments in the sodium chloride region. The spectra of methylacetoxysilanes showed a typical ester absorption similar to that of organic esters, but the spectra of all the dimethyltin formates and acetates reported here showed the presence of carboxylate ions in the solid state, as shown in Table I.

Experimental

Starting Materials.—Dimethyltin dichloride (m.p. 106°) was supplied by the Metal and Thermit Corporation. Dimethyltin oxide was prepared by the hydrolysis of dimethyltin dichloride with aqueous ammonia and was washed repeatedly until the filtrate showed no reaction with silver nitrate.

Analyses.—Concentrated sulfuric acid (15–20 drops) was added to the sample (0.2–0.3 g.), weighed in a platinum crucible, and the mixture carefully heated until fumes of SO_3 were no longer evolved. A few drops of nitric acid were then added, and the residue was heated to red heat with a Meeker burner for fifteen minutes. The cooled residue was weighed as SnO_2, and the results are given in Table I.

Preparation of Dimethylchloroformoxystannane.—A mixture of dimethyltin dichloride (3 g.), sodium formate (0.74 g.) and formic acid (10 g.) was refluxed for one hour, then formic acid was distilled off under reduced pressure. Two sublimates, one of which melted at 105–106° (0.7 g.) and the other at 143–144° (1.7 g.), were obtained. Analysis of the latter sublimate showed that it was $(CH_3)_2SnCl(OOCH)$.

Dimethyltin dichloride was refluxed with an excess of formic acid, followed by the distillation of the acid and sublimation. The sublimate consisted of unreacted dimethyltin dichloride. No higher melting compound was found.

Tetramethyl-1,3-dichlorodistannoxane (0.9 g.) was dissolved in formic acid (9 g.) at its refluxing temperature and, after being refluxed ten minutes, the excess acid was distilled off under reduced pressure. Large crystals remained in the flask. A sublimate melting at 142–144° (1 g.) and a small amount of residue were obtained; the sublimate was dimethylchloroformoxystannane (see Table I). This reaction seemed to be carried out almost quantitatively. With acetic acid, tetramethyl-1,3-dichlorodistannoxane was also cleaved easily to give dimethylchloroacetoxystannane.

Preparation of Dimethyldiformoxystannane.—A mixture of dimethyltin dichloride (3 g.), sodium formate (2 g.) and formic acid (10 g.) was refluxed for a few hours, then submitted to distillation and sublimation under reduced pressure. The sublimate consisted of two fractions: m.p. 160–185° (0.4 g.) and m.p. 185° (2.3 g.), the latter being $(CH_3)_2Sn(OOCH)_2$.

Dimethyltin oxide (2 g.) was dissolved in formic acid (1 g.) and refluxed for a short time. Excess acid was taken off. A sublimate of dimethyldiformoxystannane (1.9 g., m.p. 184–185°) and a small amount of residue were obtained. Dimethyldiformoxystannane hydrolyzes easily, and recrystallization from methanol usually gave polymeric α,ω-diformoxydimethylstannoxane $(HCOO)[(CH_3)_2SnO]_n(OCH)$ owing to partial hydrolysis.

Preparation of Dimethylchloroacetoxystannane.—A mixture of dimethyltin dichloride (15 g.) and acetic anhydride (40 g.) was refluxed six hours, followed by distillation of the excess anhydride. The crystalline product was sublimed under reduced pressure, and three fractions were obtained: m.p. 105–107° (4 g.), m.p. 107–177° (0.8 g.), m.p. 184–189° (8.5 g.), and 1 g. of residue. From the melting point, the first fraction seemed to be unreacted dimethyltin dichloride. The third fraction was purified again by sublimation, and crystals of dimethylchloroacetoxystannane which melt at 189° were obtained. The results of analysis are shown in Table I. The residue was heated under 1 mm. pressure, but no sublimate was obtained up to 150°.

Dimethyltin dichloride (15 g.) and glacial acetic acid (30 g.) gave a small amount (2 g.) of crude dimethylchloroacetoxystannane.

Preparation of Tetramethyl-1,3-dichlorodistannoxane.—Dimethylchloroacetoxystannane (2.4 g.) was dissolved in a mixture of methanol (50 g.) and water (1 g.). After two hours of refluxing, the mixture was evaporated on a hot plate. Analysis of the residue showed that hydrolysis was incomplete; the tin content was 57.26% instead of the 61.75 % calculated for $Cl_2(CH_3)_4Sn_2O$. Furthermore, the infrared spectrum showed clearly the presence of residual acetate ion. Further refluxing in ethanol and a small amount of water gave a solid which had a tin content of 61.30% and which had no acetate ion absorption. Recrystallization from benzene gave crystals which did not melt under 300° but became yellow at 300°. The crystals dissolved in hot concentrated sulfuric acid with the evolution of hydrogen chloride. This compound could not be sublimed, but on prolonged heating under 1 mm. pressure a small amount of sublimate (m.p. 107°) was obtained. This seemed to be dimethyltin dichloride (reported[6] m.p. 106°) formed by decomposition.

Dimethyltin oxide (1.5 g.) was suspended in boiling methanol and concentrated hydrochloric acid was dropped in until a clear solution was obtained. Methanol was evaporated and sublimation gave dimethyltin dichloride (0.7 g.) and crude tetramethyl-1,3-dichlorodistanoxane (0.5 g.). Dimethyltin dichloride (m.p. 108°) thus obtained has no unpleasant smell such as is characteristic of crude dimethyltin dichloride prepared in other ways, and the tin content of 54.00% agreed well with the calculated value of 54.03% for $(CH_3)_2SnCl_2$. It may well be that the correct melting point of dimethyltin dichloride therefore should be 108°.

TABLE I

DIMETHYLTIN DERIVATIVES

Compound	M.p., °C.	Tin, % Calcd.	Tin, % Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Positions of CO_2 stretching vibration (cm.$^{-1}$) Antisymm.	Positions of CO_2 stretching vibration (cm.$^{-1}$) Symm.
$Cl(CH_3)_2SnR$									
R = OOCH	143	51.78	51.74	15.72	15.50	3.08	3.31	1595	1375
R = $OOCCH_3$	189	48.79	48.80	19.75	19.63	3.73	3.63	1564	1413
$(CH_3)_2Sn(OOCH)_2$	185	49.71	49.70	20.12	20.41	3.38	3.82	1588	1390
$R(CH_3)_2SnOSn(CH_3)_2R$									
R = Cl	..	61.75	61.75	12.50	12.27	3.15	3.18	..	..
R = $OOCCH_3$	240	55.01	54.97	22.26	22.46	4.20	4.17	1580	1410

Preparation of Tetramethyl-1,3-diacetoxydistannoxane.—A mixture of dimethyltin oxide (4 g.) and acetic anhydride (25 g.) was refluxed for one hour, followed by distillation of the excess anhydride with 20–30 cc. of xylene. From the methanol solution of the product, which was evaporated on a hot plate, three portions of crystals amounting to 2 g., 1 g. and 1 g. were obtained. The first two portions of these crystals melted at 236–237°. The same substance was obtained when dimethyltin oxide was allowed to react with glacial acetic acid or 50% aqueous acetic acid. Recrystallization from methanol. by adding a small amount of acetic acid, gave crystals which melted at 240° and then frothed up to leave a waxy solid and a small amount of crystalline sublimate. The results of analyses of both preparations are given in Table I. Sublimation was not considered to be a suitable method to obtain a pure compound because of contamination with some decomposition products even under 1 mm. pressure.

Attempts to Obtain Dimethyldiacetoxystannane.—A reaction of dimethyltin dichloride and acetic acid with sodium acetate was carried out, but the product decomposed even when sublimation was carried out under 1 mm. pressure. A small amount of sublimate (m.p. 233°) seemed to be a dimeric compound which had a pungent acetic smell.

Tetramethyl-1,3-diacetoxydistannoxane (3.7 g.) was allowed to react with an excess of acetic anhydride. During the course of sublimation, a large wet crystalline sublimate (2.5 g.) was obtained. These crystals had a pungent acetic smell, turned white on exposure to air and melted at an indefinite temperature. Recrystallization from benzene gave a product composed mainly of the distannoxane. The reaction of dimethylchloroacetoxystannane with an excess of acetic anhydride did not give the desired compound.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

The Infrared Spectra of the Methylacetoxysilanes and Some Methyltin Carboxylates. The Configuration of the Trimethyltin and the Dimethyltin Cations

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The infrared spectra of trimethylacetoxysilane, dimethyldiacetoxysilane, methyltriacetoxysilane and silicon tetraacetate have been examined over the range 1000–3500 cm.$^{-1}$. Trimethyltin acetate, formate, chloroacetates, propionate and halides, dimethyltin acetate, formate and halides and monomethyltin halides have also been studied over the range 400–3500 cm.$^{-1}$. The spectra of the silicon acetates are very similar to those of organic acetates, and it is concluded that the bonding is similar to that of an organic ester. The spectra of the tin acetate and other tin derivatives, on the other hand, show the presence of the carboxylate anion. Characteristic vibrations of the methyl-tin groups are found near 780 and 1200 cm.$^{-1}$. The trimethyltin cation is found to have a planar structure, and the dimethyltin cation is linear.

The methylacetoxysilanes have been known for some time, but only recently has a variety of methyltin esters been prepared.[3] As there is now an increasing interest in the organic derivatives of tin, we report the results of this comparative study of the infrared spectra of 24 compounds.

TABLE I

	M.p., °C.	Anal., calcd. Sn	Anal., calcd. C	Anal., calcd. H	Anal., found Sn	Anal., found C	Anal., found H
$(CH_3)_3SnOOCH$	151	56.84	23.01	4.83	56.88	23.37	4.83
$(CH_3)_3SnOOCCH_3$	197[a]	53.27	26.95	5.43	53.39	26.75	5.56
$(CH_3)_3SnOOCCH_2Cl$	148	46.13	23.34	4.31	46.21	23.79	4.71
$(CH_3)_3SnOOCCHCl_2$	135	40.69	20.58	3.46	40.87	20.84	3.75
$(CH_3)_3SnOOCCCl_3$	179	36.39	18.41	2.78	36.37	18.41	2.67
$(CH_3)_3SnOOCC_2H_5$	136		30.42	5.96		30.28	6.01
$(CH_3)_3SnF$		64.93	19.71	4.96	64.94	19.73	4.76

[a] Lit.[5] 196.5–197.5°.

Experimental

The methylacetoxysilanes and silicon tetraacetate were prepared by the reaction of the corresponding methylchlorosilane or silicon tetrachloride with acetic anhydride.[4]

Trimethyltin salts other than the fluoride were obtained by the reaction of trimethyltin hydroxide and the corresponding acid, followed by purification by sublimation. The fluoride was prepared by neutralization of trimethyltin hydroxide with 50% hydrofluoric acid and was recrystallized. Melting points and analyses are given in Table I.

The preparation of the dimethyltin derivatives has been reported.[3] Dimethyltin and methyltin halides were obtained by the reaction of the hydrohalogen acid with dimethyltin oxide or methylstannoic acid. All the halides, except the fluoride, were identified by their melting points.

The infrared absorption spectra were recorded using a Perkin–Elmer (Model 21) double-beam spectrophotometer equipped with NaCl or KBr[6] optics. Spectra were calibrated using known peaks of a polystyrene film or of 1,3,5-trichlorobenzene.

The spectra of the silicon acetates are those of solutions in carbon tetrachloride. In the NaCl region, the spectra of the methyltin halides, except the fluoride, are those of solutions in carbon tetrachloride and carbon disulfide. The other tin derivatives were insoluble, and the spectra were obtained using pressed KBr discs. In the KBr region, pure liquid, Nujol mull, and KBr discs were used.

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[1] Research Fellow in Chemistry at Harvard University, 1958–1959.

[2] Research Fellow in Chemistry at Harvard University, 1958–1959.

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[6] We thank Dr. Nakamoto of Clark University, Worcester, Mass., for the use of his spectrophotometer equipped with KBr optics.