The Reaction of Dimethyltin Dichloride with Carboxylic Acids and Phenols in an Aqueous Solution

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The reaction of dimethyltin dichloride in an aqueous solution with various inorganic and organic compounds has previously been reported by Rochow, Seyferth and Smith,¹⁾ and the reaction with acetic acid anhydride or glacial acetic acid has also been studied by Okawara and Rochow.¹,²⁾

In this paper the reaction of dimethyltin dichloride with carboxylic acids and phenols in an aqueous solution will be described. In reactions with the acids and phenols shown in Table I, precipitation occurs only when deprotonating reagents such as concentrated aqueous ammonia are added. The precipitates are recrystallized from methanol containing a small amount of the corresponding acid or phenol in order to prevent decomposition, thus yielding tetramethyl-1, 3-di(substituted)-distannoxanes. These products all have a strong, and characteristic absorption near 600 cm^{-1}, as is shown in Table I, an absorption which has previously been assigned to the Sn-O-Sn stretching vibration in polymeric⁴⁾ or dimeric³,⁵⁾ compounds.

In the reaction with benzoic acid, the initial precipitate seems to be tetramethyl-1, 3-dibenzoyloxydistannoxane. However, recrystallization from methanol containing a small amount of benzoic acid gives large colorless crystals of $(CH_3)_2Sn(C_6H_5CO_2)_2$, which melts at 162—164°C. Reaction with catechol, mercaptoacetic acid or oxalic acid gives a precipitate without deprotonating reagents. The products are $(CH_3)_2Sn(C_6H_4O_2)$, $(CH_3)_2Sn(SCH_2CO_2)$ and $(CH_3)_2Sn(C_2O_4)\cdot H_2O$ respectively. Because of their poor solubility in non-polar solvents, the molecular weight of these three compounds, as well as those of the other distannoxanes shown in Table I, were not determined.

In the case of resorcinol, hydroquinone or malonic acid, precipitation does not occur by mixing in an aqueous solution of the reagents, but a precipitate can be obtained by adding concentrated aqueous ammonia. However, the products are not simple and, therefore, can not be characterized.

Experimental

Starting Materials. — Crude dimethyltin dichloride was purified by recrystallization from benzene¹⁾ or by sublimation.²⁾ Carboxylic acids and phenols commercially obtained were used without further treatment.

Infrared Spectra*.—The infrared spectra in the 5000—400 cm^{-1} region were recorded in Nujol mull using a Hitachi-EPI-2G spectrophotometer with gratings. The positions of the bands associated with the Sn-O-Sn stretching vibration are listed in Table I.

Tetramethyl-1, 3-diformoxy-distannoxane.—To a solution of dimethyltin dichloride (5 g. 0.023 mol.) and formic acid (4 g. 0.087 mol.) in 100 ml. of water, concentrated aqueous ammonia was stirred in drop by drop until no additional precipitate was formed. The precipitate was then washed with dilute aqueous formic acid, and then by a small amount of methanol, and dried in vacuo. Recrystallization from methanol containing a small amount of formic acid gave large colorless crystals which melted at 185°C, as is shown in Table I. The analysis for tin content was carried out in a manner already described elsewhere.²⁾

The other compounds shown in Table I were prepared by a similar procedure in a good yield (70—80%). However, the *o*-methoxyphenoxy compound could be recrystallized from methanol or benzene without adding guaiacol.

Dimethyltin Dibenzoate.—To a 500 ml. of a hot aqueous solution containing 4 g. (0.018 mol.) of dimethyltin dichloride and 6 g. (0.049 mol.) of benzoic acid, concentrated aqueous ammonia was added carefully until no additional precipitate formed. The white precipitate, which was washed with hot water and methanol and dried in vacuo, seemed to be a distannoxane derivative.¹⁾

Found: Sn, 42.25. Calcd. for $C_{18}H_{22}O_5Sn_2$: Sn, 42.71%.

Recrystallization from methanol containing a small amount of benzoic acid gave large colorless crystals of dimethyltin dibenzoate. M. p. 162—164°C. (Reported⁷⁾: m. p. 160—162°C). Yield:

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1) E. G. Rochow, D. Seyferth and A. C. Smith, Jr., *J. Am. Chem. Soc.*, **75**, 3099 (1953).

2) R. Okawara and E. G. Rochow, ibid., **82**, 3285 (1960).

3) R. Okawara and M. Wada, *J. Organometal. Chem.*, **1**, 81 (1963).

4) M. P. Brown, R. Okawara and E. G. Rochow, *Spectrochim. Acta*, **16**, 595 (1960).

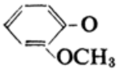
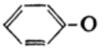
5) M. Wada and R. Okawara, to be published in *J. Organometal. Chem.*

* A discussion of the infrared spectra of these compounds will be published later.

6) W. J. Considine, J. J. Ventura, A. J. Gibbons, Jr., and A. Ross, *Can. J. Chem.*, **41**, 1239 (1963).

7) G. A. Razuvaev, O. A. Schepetkova and N. S. Vyazankin, *Zhur. Obs. Khim.*, **32**, 2152 (1962).

TABLE I. TETRAMETHYL-1,3-DI(SUBSTITUTED)DISTANNOXANES: $R(CH_3)_2SnOSn(CH_3)_2R$

R	M. p. °C	% Sn Found (Calcd.)	% C Found (Calcd.)	% H Found (Calcd.)	Sn-O-Sn Str. Vib. (cm^{-1})
HCOO	185 (decomp.)	58.79 (58.82)	17.76 (17.86)	3.60 (3.50)	612
C_2H_5COO	185	51.77 (51.64)	26.23 (26.13)	4.82 (4.82)	639
n-C_3H_7COO	161—162	48.77 (48.67)	29.29 (29.55)	5.22 (5.37)	639
CH_2ClCOO	226—227	47.64 (47.43)	19.42 (19.20)	3.25 (3.22)	636
$CHCl_2COO$	232—233	41.81 (41.69)	16.72 (16.87)	2.81 (2.48)	625
CCl_3COO	221—222	37.11 (37.19)	14.52 (15.05)	2.10 (1.90)	631
$CH_2(CN)COO$	300	49.37 (49.29)	24.86 (24.94)	3.44 (3.35)	637
CH_2BrCOO	172—174	40.32 (40.27)	16.29 (16.30)	2.92 (2.74)	636
	235—236	42.00 (42.41)	38.64 (38.62)	4.67 (4.68)	639
	202*	47.42 (47.50)	38.40 (38.45)	4.35 (4.44)	625

$R=CH_3COO$; m. p. 237°C (Reported²⁾ m. p. 240°C)

* Reported⁶⁾ m. p. 190—197°C with a crude product.

40—50%.

Found: C, 48.99; H, 3.90; Sn, 30.33. Calcd. $C_{16}H_{16}O_4Sn$: C, 49.15; H, 4.13; Sn, 30.36%.

(o-Phenylenedioxy)dimethyltin. — A white precipitate was obtained immediately by stirring in, drop by drop, 35 ml. of 10% aqueous catechol to a solution of 1.4 g. (0.0064 mol.) of dimethyltin dichloride in 50 ml. of water. After the reaction mixture had been digested on a water bath for several hours, the precipitate was filtered, repeatedly washed with hot water until the filtrate was free from chlorine, and dried at 120°C. Yield: 60%. It was purified by sublimation at 260—220°C in vacuo as has been reported.⁸⁾ The results of the analysis and of the infrared spectra in the 5000—400 cm^{-1} region of the precipitate and the sublimate were quite identical. Neither compound showed any infrared absorption bands due to O-H stretching vibrations.

Found: C, 37.42; H, 3.92; Sn, 46.20. Calcd. for $C_8H_{10}O_2Sn$: C, 37.41; H, 3.92; Sn, 46.21%.

In the methanol solution, dimethyltin dichloride and catechol produced no precipitate in spite of the insolubility of $(C_6H_4O_2)Sn(CH_3)_2$ in methanol. On the other hand, dimethyltin dichlororide produced no precipitate with resorcinol or hydroquinone in an aqueous solution.

The Reaction of Dimethyltin Dichloride with Marcaptoacetic Acid.—To a solution of dimethyltin dichloride (5.5 g. 0.025 mol.) in 50 ml. of water, 50 ml. of 15% aqueous mercaptoacetic acid was added slowly. The filtrate was then washed thoroughly with water and then by a small amount of methanol, and dried in vacuo. Yield: 75—80%. This compound could be recrystallized from a large amount of boiling water without decomposition. The infrared spectra of the precipitate and the recrystallized product could be superimposed in the 5000—400 cm^{-1} region and showed no absorption band due to the S-H or the O-H stretching vibration. The recrystalized product gradually became brown near 200°C and melted at 257—259°C.

Found: C, 20.03; H, 3.62; Sn, 49.80. Calcd. for $C_4H_8O_2SnS$: C, 20.11; H, 3.38; Sn, 49.69%.

Dimethyltin Oxalate Monohydrate.¹⁾—To 100 ml. of a 4% hot aqueous solution of dimethyltin dichloride, 100 ml. of 3% hot aqueous oxalic acid was added. The white precipitate thus obtained was digested on a steam bath for several hours, filtered, washed with hot water, and dried at 120°C. It could be recrystallized from a large amount of boiling water, but complete dehydration could not be accomplished without decomposition.

Found: C, 18.67; H, 3.12. Calcd. for $C_4H_8O_5Sn$: C, 18.85; H, 3.16%.

On the other hand, dimethyltin dichloride produced no precipitate with malonic acid in an aqueous solution.

Summary

The reactions of dimethyltin dichloride with carboxylic acids and phenols in aqueous solution have been described, and ten new compounds reported. In many cases tetramethyl-1,3-di(substituted)distannoxanes are formed in good yields by adding such deprotonating reagents as concentrated aqueous ammonia. In other cases, simple dimethyltin derivatives can be obtained without deprotonating reagents.

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8) H. J. Emeleus and J. J. Zuckerman, *J. Organometal. Chem.*, **1**, 328 (1964).