Contribution from the Department of Applied Chemistry,
Osaka University, Yamada-kami, Suita, Osaka, Japan

Preparation and Properties of Some Tin(IV) Tropolonates

M. Komura, T. Tanaka, and R. Okawara

Received July 15, 1968

A series of tin(IV) tropolonates, $(C_6H_5)_3Sn(T)$, $(CH_3)_2SnX(T)$, $R_2Sn(T)_2$, $RSnX(T)_2$, $X_2Sn(T)_2$, and $n\text{-}C_4H_9Sn(T)_3$ (R=alkyl or phenyl; X=Cl, Br or I; HT=tropolone) has been prepared. Studies of the infrared and proton nmr spectra indicate that dimethyltin bis(tropolonate) has a highly distorted octahedral configuration, and dimethyltin halide tropolonates have a trigonal bipyramidal structure probably with two methyl groups in equatorial positions. It was found that dimethyltin halide tropolonates disproportionate to methyltin halide bis(tropolonates) and trimethyltin halides at elevated temperatures.

Introduction

Tropolone[1] and its β-isopropyl derivative (hinokitiol)[2,3] react with metal ions to form stable complexes. The formation constants of several transition metal tropolonates[4] and the results of X-ray analysis on sodium[5] and copper[6] tropolonates have been reported. A hepta-coordinated structure has been suggested for phenyltin tris(tropolonate),[7] and this structure has also been assumed for *n*-butyltin tris(oxinate).[8] This paper describes the preparation and properties of a series of organotin and halogenotin(IV) tropolonates containing the penta-, hexa- or hepta-coordinated tin. For some of those, the configuration and stability will be discussed from the infrared and pmr spectra.

Experimental Section

Starting materials. Organotin halides and tin tetrahalides were purified by sublimation, recrystallization or distillation. Dimethyltin sulfide[9] and *n*-butyltin sesquisulfide[10] were prepared according to the procedures cited in the literature. Tropolone was kindly supplied by Prof. T. Mukai of Tohoku University. Sodium tropolonate was prepared by adding thin strips of sodium metal to a solution of tropolone in methanol. Copper tropolonate was prepared according to the literature.[1]

Triphenyltin tropolonate, $(C_6H_5)_3Sn(T)$. Triphenyltin chloride (0.8 g, 2 mmole) in ethanol (50 ml) was added to an ethanol solution (50 ml) of sodium tropolonate (0.3 g, 2 mmole) and the mixture was stirred for half an hour. Sodium chloride was filtered off, and the filtrate was concentrated, giving a pale yellow needle (0.8 g, 85% yield) of $(C_6H_5)_3Sn(T)$.

Dimethyltin halide tropolonates, $(CH_3)_2SnX(T)$ (X=Cl, Br). Dimethyltin dichloride (0.9 g, 4 mmole) and $(CH_3)_2Sn(T)_2$ (1.6 g, 4 mmole) were dissolved in chloroform (100 ml). The solvent was removed under reduced pressure and the residue was recrystallized from chloroform-ethanol mixture to give yellow crystals (1.4 g, 60% yield) of $(CH_3)_2SnCl(T)$. When this reaction was carried out in *refluxing* acetonitrile for 4 hours, the strong penetrating odor of $(CH_3)_3SnCl$ was recognized and a pale yellow solid (m.p. 226-229°C) was obtained (ca. 50% yield), whose infrared and nmr spectra were in accordance with methyltin chloride bis(tropolonate). The bromide, $(CH_3)_2SnBr(T)$, was prepared from $(CH_3)_2SnBr_2$ and $(CH_3)_2Sn(T)_2$ in an analogous manner. On the other hand, the iodide derivative, $(CH_3)_2SnI(T)$, was not isolated even at room temperature owing to a disproportionation.

Dialkyltin bis(tropolonates), $R_2Sn(T)_2$. Dimethyltin bis(tropolonate) was synthesized by the following two procedures: (i) Dimethyltin dichloride (1.8 g, 8 mmole) in ethanol (100 ml) was added to a suspension of sodium tropolonate (2.3 g, 16 mmole) in 100 ml of ethanol and the mixture was stirred for half an hour. Sodium chloride was filtered off, and the filtrate was concentrated under reduced pressure. The crude product obtained was recrystallized from hot ethanol, giving pale yellow crystals (2.6 g, 84% yield) of $(CH_3)_2Sn(T)_2$. (ii) Dimethyltin sulfide (0.9 g, 5 mmole) and tropolone (1.2 g, 10 mmole) were dissolved in ethanol (100 ml) and the solution was refluxed for three hours. After evolution of hydrogen sulfide was ceased, the solution was concentrated under reduced pressure, giving $(CH_3)_2Sn(T)_2$ (1.9 g, 97% yield). Other dialkyl- and diphenyltin bis(tropolonates) were prepared in an analogous manner.

Alkyltin halide bis(tropolonates), $RSnX(T)_2$. Methyltin oxide (0.5 g, 3 mmole) was dissolved in the

---

(1) J. W. Cook, A. R. Gibb, R. A. Raphael, and A. R. Somerville, *J. Chem. Soc.*, 503 (1951).

(2) T. Nozoe, *Bull. Chem. Soc. Japan*, *11*, 295 (1936).

(3) H. Iinuma, *J. Chem. Soc. Japan*, *64*, 742, 901 (1943).

(4) B. E. Bryant, W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, *75*, 3784 (1953).

(5) Y. Sasada and I. Nitta, *Acta Cryst.*, *9*, 205 (1956).

(6) J. M. Robertson, *J. Chem. Soc.*, 1222 (1951).

(7) E. L. Muetterties and C. M. Wright, *J. Am. Chem. Soc.*, *86*, 5132 (1964).

(8) K. Kawakami, Y. Kawasaki, and R. Okawara, *Bull. Chem. Soc. Japan*, *40*, 2693 (1967).

(9) W. T. Reichle, *J. Org. Chem.*, *26*, 4634 (1961).

(10) M. Komura and R. Okawara, *Inorg. Nucl. Chem. Letters*, *2*, 93 (1966).

equimolar amount of dilute hydrochloric acid and an ethanol solution (50 ml) of tropolone (0.7 g, 6 mmole) was added with stirring. The pale yellow precipitate formed immediately was filtered and recrystallized from acetone-ethanol mixture to give yellow crystals (1.0 g, 83% yield) of $CH_3SnCl(T)_2$. Other alkyltin halide bis(tropolonates) were prepared analogously.

n-Butyltin tris(tropolonate), n-$C_4H_9Sn(T)_3$. n-Butyltin sesquisulfide (0.45 g, 2 mmole) and tropolone (0.73 g, 6 mmole) were dissolved in dioxane (100 ml) and refluxed for 10 hours. The pale yellow precipitate obtained was filtered and recrystallized from dioxane-ethanol mixture to give n-$C_4H_9Sn(T)_3$ (0.85 g, 80% yield).

Dihalogenotin bis(tropolonates), $X_2Sn(T)_2$ ($X = Cl, Br, I$). A benzene solution (50 ml) of tin tetrachloride (0.9 g, 3.5 mmole) was added to a solution of tropolone (0.9 g, 7 mmole) in benzene (50 ml) with stirring. The pale yellow precipitate formed immediately was filtered and washed with benzene to give $Cl_2Sn(T)_2$ (1.1 g, 73% yield). The bromide derivative was prepared from tin tetrabromide by the analogous procedure. The iodide derivative was synthesized as follows: Tin tetraiodide (1.3 g, 2 mmole) and sodium tropolonate (0.6 g, 4 mmole) were mixed in chloroform (100 ml) with stirring. The yellow precipitate obtained was washed with ether and dried to give $I_2Sn(T)_2$ (0.7 g, 60% yield).

Dihalogenotin bis(tropolonates) shown in Table I do not melt or decompose below 250°C and scarcely soluble in organic solvents. The other tropolonates are soluble in organic solvents.

Molecular weights. Molecular weights of some representative complexes were determined in chloroform by a Mechrolab vapor pressure osmometer. As is shown in Table I, the observed molecular weigths for all examined tropolonates are slightly lower than the calculated ones. This may be due to partial ionic dissociation of the complexes. However, these complexes are essentially monomeric in chloroform.

Infrared and nmr Spectra. Infrared and nmr spectra were measured as described in the previous paper.[11]

Table I. Organotin and Halogenotin Tropolonates: $(C_6H_5)_3Sn(T)$, $(CH_3)_2SnX(T)$, $R_2Sn(T)_2$, $RSnX(T)_2$, $X_2Sn(T)_2$, and n-$C_4H_9Sn(T)_3$ (R = alkyl or phenyl; X = Cl, Br or I; HT = tropolone)

		m.p. (°C)	Sn (%) Found (Calcd.)	C (%) Found (Calcd.)	H (%) Found (Calcd.)	Mol. Wt. Found (Calcd.)
$(C_6H_5)_3Sn(T)$		142-143	25.12 (25.19)	63.69 (63.74)	4.53 (4.28)	431 (471)
$(CH_3)_2SnX(T)$						
X = Cl		111-113		35.95 (35.40)	3.62 (3.63)	304 (305)
Br		85-88		31.16 (31.08)	3.20 (2.61)	
$R_2Sn(T)_2$						
R = CH_3		181-183	30.31 (30.36)	48.83 (49.15)	4.17 (4.12)	384 (391)
C_2H_5		175-176	28.39 (28.32)	51.88 (51.59)	4.88 (4.81)	392 (419)
n-C_3H_7		115-117	26.55 (26.55)	53.65 (53.73)	5.72 (5.41)	
n-C_4H_9		110-111.5	25.14 (24.98)	55.70 (55.61)	6.22 (5.94)	457 (475)
C_6H_5		224-227	23.34 (23.04)	60.38 (60.62)	3.72 (3.91)	
$RSnX T)_2$						
R = CH_3,	X = Cl	228-230	28.38 (28.85)	43.85 (43.79)	3.16 (3.19)	399 (411)
CH_3,	Br	228-230		39.74 (39.52)	2.75 (2.87)	
n-C_4H_9,	Cl	160-162	26.13 (26.17)	47.48 (47.67)	4.52 (4.22)	434 (454)
n-C_4H_9,	Br	176-177.5	23.98 (23.84)	43.10 (43.42)	4.08 (3.85)	
C_6H_5,	Cl ^{a}	247.5-252	25.48 (25.07)			
n-$C_4H_9Sn(T)_3$		240-241.5	22.05 (22.01)	55.49 (55.69)	4.71 (4.49)	522 (539)
$X_2Sn(T)_2$						
X = Cl ^{a}		>250	27.58 (27.49)	37.54 (38.94)	2.46 (2.33)	
Br ^{a}		>250		32.70 (32.29)	2.13 (1.94)	
I		>250		27.74 (27.35)	1,50 (1.64)	

^{a} Ref. (7).

---

(11) J. Otera, Y. Kawasaki, and T. Tanaka, *Inorg. Chim. Acta, 1,* 294 (1967).

Results and Discussion

Infrared Spectra. The relevant infrared frequencies for tin(IV) tropolonates and the related compounds are listed in Table II. As is shown in Table II, free tropolone shows two strong bands in the 1600-1500 cm^{-1} region, while the corresponding bands for all tin(IV) tropolonates appear at 20-40 cm^{-1} lower frequencies. From the magnitude of their frequency shifts on complex formation, the higher bands can be assigned to a perturbed C=C stretching and the lower one to a perturbed C=O stretching. Moreover, these C=C and C=O stretching frequencies of the tin(IV) tropolonates are close to those of copper(II) tropolonate (Table II), which has a chelate structure with non-equivalent Cu–O bonds.[6] Thus the tin(IV) mono(tropolonates), bis(tropolonates) and tris(tropolonate) in the present study contain a penta-, hexa-, and presumably hepta-coordinated tin atoms, respectively.

Table II. Relevant Infrared Frequencies of Tin(IV) Tropolonates, cm$^{-1\,a,b}$

Compounds	ν(C=C)		ν(C=O)	ν(Sn—O)		ν(Sn—C)		ν(Sn—Cl)	
Tropolone [c]	1618 vs		1558 vs						
Cu(T)$_2$	1595 vs		1517 vs						
Cl$_2$Sn(T)$_2$	1595 vs		1517 vs	590 vs	584 vs			339 vs	328 s
Br$_2$Sn(T)$_2$	1595 vs		1515 vs	585 vs	581 vs				
I$_2$Sn(T)$_2$	1595 vs		1515 vs	579 vs	575 vs				
C$_6$H$_5$SnCl(T)$_2$	1590 vs		1511 vs	574 s	563 vs			295 vs, br	
CH$_3$SnCl(T)$_2$	1595 vs		1515 vs	574 s	562 vs	533 m		301 vs, br	
	(1598 vs)		(1515 vs)	(573 s)	(560 vs)	(540 m)			
CH$_3$SnBr(T)$_2$	1592 vs		1513 vs	575 s	561 vs	540 m			
n-C$_4$H$_9$SnCl(T)$_2$	1592 vs		1515 vs	569 s	562 vs			295 vs, br	
n-C$_4$H$_9$SnBr(T)$_2$	1594 vs		1515 vs	568 s	562 vs				
(C$_6$H$_5$)$_2$Sn(T)$_2$	1595 vs		1512 vs	556 m	547 s				
(CH$_3$)$_2$Sn(T)$_2$	1603 vs	1595 vs	1515 vs	543 s, br		529 m	513 s		
	(1597 vs)		(1512 vs)	(540 s, br)		(529 s)	(516 s)		
(C$_2$H$_5$)$_2$Sn(T)$_2$	1595 vs		1512 vs	511 vs		543 m	491 m		
(*n*-C$_3$H$_7$)$_2$Sn(T)$_2$	1595 vs		1513 vs	512 vs, br					
(*n*-C$_4$H$_9$)$_2$Sn(T)$_2$	1597 vs		1513 vs	513 vs					
(CH$_3$)$_2$SnCl(T)	1600 vs		1520 vs	548 vs, br		569 vs	521 m	281 vs, br	
	(1600 vs)		(1517 vs)	(556 vs)		(563 vs)	(523 m)		
(CH$_3$)$_2$SnBr(T)	1600 vs		1515 vs	548 vs, br		568 vs	520 m		
(C$_6$H$_5$)$_3$Sn(T)	1597 vs		1515 vs	543 m, br					
	(1598 vs)		(1515 vs)						
n-C$_4$H$_9$Sn(T)$_3$	1592 vs		1513 vs	559 m	544 s				
	(1597 vs)		(1508 vs)	531 vs					

[a] Nujol mull, or chloroform solution in parenthesis. [b] vs, very strong; s, strong; m, medium; br, broad. [c] Carbon tetrachloride solution.

In the region of 590-510 cm^{-1}, all the tin(IV) tropolonates show characteristic strong bands which should be assigned to the Sn–O stretching vibration. In the bis(tropolonate) complexes,(*) the Sn–O stretching frequency decreases with decreasing electron-withdrawing power of substituents on the tin atom, similar to the case of bis(acetylacetonates),[13] bis-(kojates),[11] and bis-DMSO complexes[14] of tin(IV).

The Sn–O stretching frequency of tin(IV) tropo-(kojate)[11] and dimethyltin bis(dithiocarbamate).[19] In

lonates (590-510 cm^{-1}) is much higher than that of tin(IV) acetylacetonates[13] and therefore the tropolonates are expected to have rather higher covalency of the Sn–O bond than that of the acetylacetonates.

Configurations of Dimethyltin Bis(tropolonate) and Dimethyltin Halide Tropolonates. As shown in Table II, (CH$_3$)$_2$Sn(T)$_2$, (CH$_3$)$_2$SnCl(T), and (CH$_3$)$_2$SnBr(T) show two Sn–C stretching bands. This suggests that the C–Sn–C moiety is non-linear in these complexes. The spin-spin coupling constants for the tropolonates shown in Table III are much smaller than those for dimethyltin aquo-cation or dimethyltin bis(acetylacetonate) which have been reported[15,16] to have a *trans*-octahedral structure with linear C–Sn–C moiety, and comparable to those for dimethyltin bis(oxinate).(*) Thus dimethyltin bis(tropolonate) may be included in a category of a highly distorted octahedral structure which has been assumed for dimethyltin diacetate,[18] dimethyltin bis-(CH$_3$)$_3$SnCl-pyridine adduct[20] and [(CH$_3$)$_2$SnCl$_3$]$^-$[(CH$_3$)$_2$SnCl, terpyridyl]$^+$,[21] it has been known that the less electronegative methyl groups occupy equatorial positions in their trigonal bipyramidal structures in the solid state. From this analogy, dimethyltin halide tropolonates are considered to have a trigonal bipyramidal structure with two methyl groups in

---

(*) There is a linear relationship between the Sn—O stretching frequencies and the sum of σ^* values[12] of the substituents, except for diethyl-, di-*n*-propyl- and di-*n*-butyltin *bis*(tropolonates).

(12) «Steric Effects in Organic Chemistry», edited by M. S. Newman, John Wiley and Sons, Inc., New York, N.Y. (1956).

(13) Y. Kawasaki, T. Tanaka, and R. Okawara, *Spectrochim. Acta, 22,* 1571 (1966).

(14) T. Tanaka, *Inorg. Chim. Acta, 1,* 217 (1967).

(*) In solid state, C—Sn—C bond angle is 110.7°.[17]

(15) M. M. McGrady and R. S. Tobias, *Inorg. Chem.*, 3, 1157 (1964).

(16) M. M. McGrady and R. S. Tobias, *J. Am. Chem. Soc.*, *87*, 1909 (1965).

(17) E. O. Schlemper, *Inorg. Chem.*, 6, 2012 (1967).

(18) Y. Maeda, C. R. Dillard, and R. Okawara, *J. Organometal. Chem.*, *10*, 247 (1967).

(19) M. Honda, M. Komura, Y. Kawasaki, T. Tanaka, and R. Okawara, *J. Inorg. Nucl. Chem.*, in press.

(20) R. Hulme, J. Chem. Soc., 1524 (1963).

(21) F. W. B. Einstein and B. R. Penfold, *Chem. Comm.*, 780 (1966).

Table III. Tin Proton Coupling Constants and Proton Chemical Shifts for Several Methyltin Compounds

Compound	$J(^{117}Sn—CH_3)$ (c.p.s.)	$J(^{119}Sn—CH_3)$ (c.p.s.)	$\tau(Sn—CH_3)$ [a] (p.p.m.)	Solvent
$(CH_3)_2Sn(T)_2$	69.2	72.2	9.52	$CHCl_2CHCl_2$
$(CH_3)_2SnCl(T)$	74.7	78.0	8.99	$CHCl_2CHCl_2$
$(CH_3)_2SnBr(T)$	73.8	77.2	8.86	$CHCl_2CHCl_2$
$(CH_3)_2SnI(T)$ [b]	71.7	74.7	8.72	$CHCl_2CHCl_2$
$[(CH_3)_2Sn(aq)]^{2+}$ [c]	102.0	107.0		H_2O
$(CH_3)_2Sn(acac)_2$ [c]	95.0	99.3	9.51	$CDCl_3$
$(CH_3)_2Sn(Ox)_2$ [c]	67.9	71.2	9.56	$CDCl_3$

[a] $\tau_{tetramethylsilane} = 10.0$. [b] Measured for assolution containing the equimolar mixture of $(CH_3)_2SnI_2$ and $(CH_3)_2Sn(T)_2$. [c] Ref. (16).

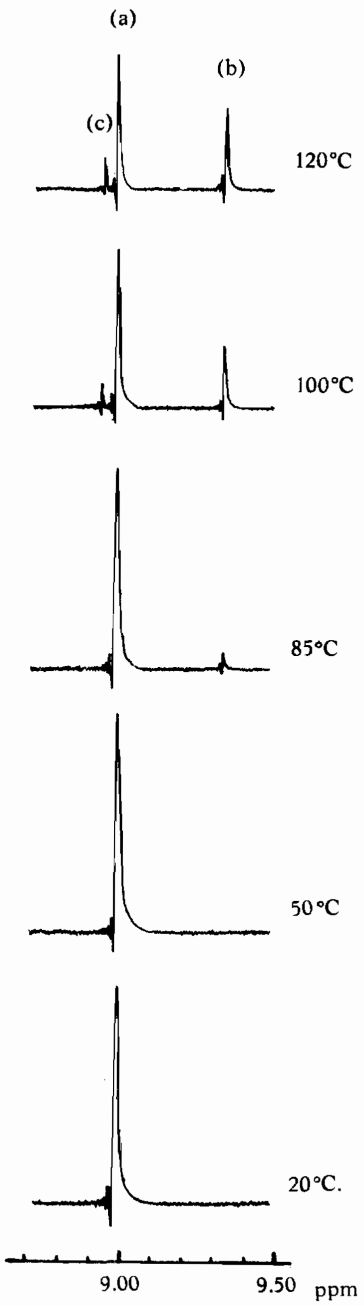

Figure 1. Temperature-dependent pmr spectra for the equimolar $(CH_3)_2SnCl_2$—$(CH_3)_2Sn(T)_2$ in 1,1,2,2-tetrachloroethane. (a) $(CH_3)_2SnCl(T)$, (b) $(CH_3)_3SnCl$, and (c) $CH_3SnCl(T)_2$.

equatorial positions, although it may be more or less distorted. This configuration is consistent with the results of infrared and pmr spectra in the solid state or in solution.

Tin-Carbon Bond Cleavage in Dimethyltin Halide Tropolonates. As described in experimental section, dimethyltin halide tropolonates disproportionate to methyltin halide bis(tropolonates) and trimethyltin halides, analogous to dialkyltin halide oxinates.[22] This reaction is also confirmed by nmr measurements.

As shown in Figure 1, when an equimolar amounts of $(CH_3)_2SnCl_2$ (τ, 8.73 ppm in $CHCl_2CHCl_2$) and $(CH_3)_2Sn(T)_2$ were dissolved at room temperature, the spectrum shows only one methyl proton signal (9.00 ppm), which can be assigned to $(CH_3)_2SnCl(T)$, but no signals of the starting materials. Although the spectrum does not change in the temperature range 20-80°C, the signal of $(CH_3)_3SnCl$ (9.34 ppm) begins to appear at 85°C. Above 100°C, a signal of $CH_3SnCl(T)_2$ (8.96 ppm) can also be observed. Thus it is suggested that the reaction (1) proceeds completely at room temperature, and is followed by the disproportionation reaction (2) at elevated temperatures. This mechanism may be supported from that the nmr measurements on starting from the $(CH_3)_2SnX(T)$ compound agreed with that on an equimolar mixture of $(CH_3)_2Sn(T)_2$ and $(CH_3)_2SnX_2$.

$$(CH_3)_2Sn(T)_2 + (CH_3)_2SnX_2 \xrightarrow{\text{Room temp.}} 2(CH_3)_2SnX(T) \qquad (1)$$

$$2(CH_3)_2SnX(T) \longrightarrow CH_3SnX(T)_2 + (CH_3)_3SnX \qquad (2)$$

(T = tropolonate; X = Cl, Br or I)

The failure to prepare $(CH_3)_2SnCl(T)$ in *refluxing* acetonitrile described in the experimental section could be understood by these observations.

At room temperature, $(CH_3)_2SnCl(T)$ seems to be very stable in solution and the reaction (2) does not proceed within several months. Similar behaviour was observed on the equimolar mixture of $(CH_3)_2SnBr_2$ and $(CH_3)_2Sn(T)_2$. In the case of the iodide, however, the reaction (2) proceeds to a considerable extent within several hours even at room temperature, showing an example of the instability of a pentacoordinated tin.

---

(22) K. Kawakami and R. Okawara, *J. Organometal. Chem.*, 6, 249 (1966).