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Syntheses and Characterization of Tributyltin(IV) Carboxylates Containing ∝-Oxoketene Cyclic Dithioacetals

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ABSTRACT

Five aquatributyltin-2-(dialkylthio)methylene-3-oxo-5-aryl-4-pentenoates (3) were synthesized and characterized by IR spectra, ¹H NMR spectra, ¹³C NMR spectra and elemental analyses. The IR spectra of (3) show strong O—H stretching modes in the region of 3384-3455 cm⁻¹. In the ¹H NMR spectra of (3), signals due to the protons of an α -oxoketene dithioacetal segment shift upfield compared to those of free acids (2). This is indicative of the formation of the tin ester complexes. The

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structure of $4-O_2N-C_6H_4CH=CHCOC(C_3H_4S_2)CO_2Sn(C_4H_9)_3\cdot(H_2O)$ (**3d**) was determined by X-ray diffraction and showed two molecules in an asymmetric unit cell. The tin(IV) is coordinated with three carbon atoms, an oxygen of carboxylate and an oxygen of water and forms a fivecoordinate, distorted trigonal bipyramidal configuration. There is no intermolecular O—Sn coordination in (**3d**), but a molecule of water acts as one of the five ligands and coordinates directly to the tin atom. The tin—oxygen (water) bond distance in (**3d**) is discussed in relation to that in other aquatin(IV) complexes.

Key Words: Tributyltin (IV) carboxylates; α -Oxoketene cyclic dithiocetals; Coordinating water; Structure.

INTRODUCTION

Organotin compounds have been extensively studied because of their biological activities. In general, the fungicidal and antibacterial properties of organotins in vitro have indicated that the order of activity is related to the number of R groups attached to a tin atom. The order of activity has been oberved to be: $RSnX_3 < R_2SnX_2 < R_3SnX$. The nature of the X group has relatively little influence on the fungicidal activity of an organotin compound.^[1] However, studies have continued on the structures of various triorganotin com-pounds, especially containing X groups which themselves have some biological activities.^[2–5] α -Oxoketene dithioacetals and related compounds are versatile synthons in organic synthesis,^[6–8] and then some of them have been found to possess strong biological activities. In order to study the relationship between structures and activities, we have prepared herein five new tributyltin(IV) carboxylates containing an α -oxoketene cyclic dithioacetal moiety.

In organotin compounds, R_3SnO_2CR' , the coordination environment of the tin atom is normally determined by its spacial factors (volume) of the substitute groups R and R' and the electronic factors of R'.^[9–11] Thus, the study on the structure of triorganotin carboxylates is mainly embodied on the alternation of R and R' groups. In addition to the study of their biological activities, we are also interested in the nature of the bond and bond-structure in these compounds. In the present paper, the preparation and characterization of 2-(1,2-ethylenedithio)methylene-3-oxo-5-aryl-4-pentenoic acids (**2a**)–(**2e**) and the corresponding tin esters, that is, aquatributyltin(IV)-2-(dialkylthio)methylene-3-oxo-5-aryl-4-pentenoates (**3a**)– (**3e**) are described.

EXPERIMENTAL

Materials and Methods

All operations were carried out under moisture-free conditions. All solvents were dried by standard methods. ¹H NMR spectra were recorded on a Bruker Ac-80 spectrometer operating at 80 MHz and ¹³C NMR spectra were recorded on a Varian XL-400 spectrometer operating at 100 MHz with TMS as internal reference and chloroform-*d* as solvent. IR spectra were recorded on a BIDF TS-135 FT-IR spectrophotometer with KBr pellets. Elemental analyses were taken with a Bio-Rad Co. elemental analytical instrument.

Acyl (Alkoxycarbonyl)ketene Dithioacetal (1)

To a well-stirred suspension of ethyl acetoacetate (13.00 g, 0.10 mol) and anhydrous potassium carbonate (42.00 g, 0.30 mol) in N,N-dimethylformamide (50 mL) was added carbon disulfide (9.00 mL, 0.15 mol) at room temperature. To this reaction mixture was added drop-wise over 30 min 1,2-dibromoethane (10.30 mL, 0.12 mol). Stirring was continued another 7 h at room temperature. Ice water (150 mL) was added until precipitating a yellow product, which was recrystallized from ethanol to give (1) (21.20 g, 91.50%), m.p. 79.0–81.0 °C. ¹H NMR (δ , CDCl₃): 1.37 (t, 3H, J = 8.0 Hz, CH₃-CH₂-O-); 2.40 (s, 3H, CH₃-); 3.30 (s, 4H, 2 × -SCH₂-); 4.33 (q, 2H, J = 8.0 Hz, -O-CH₂-CH₃).

2-(1,2-Ethylenedithio)methylene-3-oxo-5-aryl-4-pentenoic Acids (2)

Compounds (2) were prepared according to a literature method.^[12]

General procedure. To a solution of arylaldehyde (10 mmol) and (1) (2.32 g, 10.0 mmol) in ethanol (50 mL), sodium ethoxide (11 mmol, 0.25 g sodium dissolved in 5 mL ethanol) was added drop-wise. After that the reaction mixture was stirred at room temperature overnight. Then the mixture was poured into cold water (ca. 100 mL). The resulting precipitate was collected and washed with water. The pure product was obtained by recrystallization from ethanol.

For the characterization of (2a)-(2c) see Ref. [12].

(2d) Yellow crystals, yield: 3.15 g (93.4%), m.p. 156.0–158.0 °C (dec). *Anal.* Calcd. for $C_{14}H_{11}NO_5S_2$ (MW 337.37): C, 49.85; H, 3.26; N, 4.15%. Found: C, 49.92; H, 3.33; N, 4.02%. ¹H NMR (δ , DMSO- d_6): 3.43 (s, 4H, 2 × -SCH₂-), 7.14 (d, 1H, J = 16.0 Hz, Ar-CH=CHCO), 7.58 (d,

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1H, d, J = 16.0 Hz, Ar-CH=CHCO), 7.93 (d, 2H, J = 8.8 Hz, Ar-H), 8.24 (d, 2H, J = 8.8 Hz, Ar-H), 11.25 (1H, s(br), OH).

(2e) Yellow crystals, yield: 2.80 g (99.2%), m.p. 151.0-153.0 °C (dec). Anal. Calcd. for C₁₂H₁₀O₄S₂ (MW 282.34): C, 51.06; H, 3.55%. Found: C, 51.11; H, 3.68%. ¹H NMR (δ , CDCl₃): 3.45 (s, 4H, 2 × -SCH₂-), 6.49 (m, 1H, 4-furanyl-H), 6.59 (d, 1H, J = 15.4 Hz, Ar-CH=CHCO), 7.25–7.50 (m, 3H, Ar-CH=CHCO + 3,5-furanyl-H), OH not observed.

Synthesis of Tributyltin(IV) Carboxylates (3)

All compounds (3a)-(3e) were synthesized using similar procedures, respectively, and a general procedure is described. A mixture of $(n-Bu_3Sn)_2O$ (0.359 g, 1.2 mmol) and (2) (1.0 mmol) and benzene (20 mL) was refluxed for 4.5 h with stirring. The water liberated in the reaction was removed azeotropically by a Dean-Stark apparatus. Then the mixture was cooled to 40 °C and benzene was removed under reduced pressure. The resulting residue was purified by silica gel (80–120 mesh) chromatography (petroleum ether:ethyl acetate = 1:2 (V/V) as an eluent) to give a pure product.

X-Ray Crystallography

Yellow crystals of (**3d**) obtained from a mixture solution of petroleum ether and diethyl ether were suitable for a single-crystal X-ray diffraction study. Diffraction intensities were collected on a Siemens P4 diffractometer fitted with graphite-monochromated MoK α radiation $\lambda = 0.71073$ Å, employing an ω -2 θ scan technique. Lorentz polarization and absorption corrections were applied.^[13] The structure was solved by direct methods using the SHELXS 86 program^[14] and refined with a fullmatrix least-squares techniques using the SHELXL 93 program.^[15] Nonhydrogen atoms were refined anisotropically. The hydrogen atoms on carbon atoms were generated geometrically, while the aqua hydrogen atoms were not located.

RESULTS AND DISCUSSION

Synthesis

2-(1,2-Ethylenedithio)methylene-3-oxo-5-aryl-4-pentenoic acids (2) were synthesized by condensation of acetylketene dithioacetal (1) with aryl aldehydes (Figure 1). Pak and co-workers had described the mechanism for the formation of (2).^[12] The esterification reaction between (2)



Figure 1. Preparation of aquatributyltin-2-(dialkylthio)methylene-3-oxo-5-aryl-4-pentenoates.

and *bis*(tri-*n*-butyltin)oxide was performed in refluxing benzene, and the tri*n*-butyltin esters (**3**) were produced in moderate to high yields (Figure 1 and Table 1). All the compounds synthesized were characterized by their IR spectra (Table 2), ¹H NMR spectra and ¹³C NMR spectra (Table 3). The study on the properties of (**3**) is in progress.

 Table 1.
 Yields and elemental analyses of (3).

	Formula	State	M.p. (dec) (°C)	Yield (%)	Elemental analysis found (calcd) (%)	
No.					С	Н
(3a)	$C_{26}H_{40}O_4S_2Sn$	Yellow oil	_	75.2	52.17	6.69
(3b)	$C_{27}H_{44}O_5S_2Sn$	Red oil	_	82.7	(32.20) 51.43 (52.31)	(6.79) 6.98 (6.76)
(3c)	$C_{27}H_{40}O_6S_2Sn$	Yellow crystals	51.0-52.0	69.8	50.39 (50.77)	6.23 (6.46)
(3d)	$C_{26}H_{39}NO_6S_2Sn$	Yellow crystals	68.0-69.0	58.2	48.52 (48.84)	6.07 (6.21)
(3e)	$C_{24}H_{38}O_5S_2Sn$	Red oil	-	66.4	48.99 (49.21)	6.46 (6.39)

No.	υ(COO) asym	υ(COO) sym	Δυ	v(Sn-C)	υ(O-H)
(3a)	1589	1318	271	495	3384
(3b)	1604	1322	282	488	3455
(3c)	1614	1358	256	490	3431
(3d)	1586	1343	243	472	3420
(3e)	1591	1327	264	498	3407

Table 2. IR data of $R^1CH=CHCOC(C_3H_4S_2)CO_2SnBu_3(H_2O)$.

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Table 3. ¹H and ¹³C NMR data for $R^1CH=CHCOC(C_3H_4S_2)CO_2SnBu_3(H_2O)$.

No.	¹ H NMR (ppm) and ¹³ C NMR (ppm)
(3a)	0.87, 9H (t, $J = 8.0$ Hz, CH ₃ -); 1.24–1.65, 18H (m, -CH ₂ -); 3.32, 4H (s, 2 × -SCH ₂ -); 7.25–7.58, 7H (m, Ar-H + Ar-CH=CHCO).
	186.6 (>C=O), 177.6 (-COO-), 170.7 (>C=), 141.0, 135.6, 129.6, 128.6,
	128.0, 125.9, 120.5 (>C=), 37.7 (-SCH ₂ -), 36.9 (-SCH ₂ -), 27.8, 27.0,
	16.8, 13.5 (-CH ₃).
(3b)	0.87, 9H (t, $J = 8.0$ Hz, -CH ₃); 1.20–1.71, 18H (m, -CH ₂ -); 3.31, 4H
	$(s, 2 \times -SCH_2-); 3.82, 3H (s, -OCH_3); 6.79-7.54, 6H (m, Ar-H +$
	Ar-C H=CH CO).
	186.4 (> C=O), 176.4 (-COO-), 170.6 (>C=),
	160.7, 140.7, 129.5, 128.1, 123.5, 120.5, 113.9 (>C=), 55.0 (-OCH ₃),
	37.5 (-SCH ₂ -), 36.7 (-SCH ₂ -), 27.6, 26.8, 16.6, 13.4 (-CH ₃).
(3c)	0.87, 9H (t, $J = 8.0$ Hz, -CH ₃); 0.95–1.21, 18H (m, -CH ₂ -); 3.31, 4H
	(s, 2 × -SCH ₂ -); 5.97, 2H (s, -OCH ₂ O-); 6.89, 1H (d, $J = 12.0$ Hz,
	Ar-CH=CHCO); 6.71–7.25, 3H (m, Ar-H); 7.42, 1H (d, $J = 12.0$ Hz,
	Ar-C H =CHCO).
	186.4 (>C=O), 176.8 (-COO-), 170.6 (>C=), 148.9,
	148.0, 140.8, 130.0, 124.2, 124.0, 121.0, 108.2, 106.3 (>C=), 101.2
	(-OCH ₂ O-), 37.6 (-SCH ₂ -), 36.8 (-SCH ₂ -), 27.7, 26.9, 16.9, 13.5 (-CH ₃).
(3d)	0.88, 9H (t, $J = 8.0$ Hz, -CH ₃); 0.97–1.55, 18H (m, -CH ₂ -); 3.35, 4H
	$(s, 2 \times -SCH_2-); 7.25-8.26, 6H (m, Ar-H + Ar-CH=CHCO).$
	185.7 (>C=O), 180.3 (-COO-), 170.5 (>C=), 147.9, 142.1, 137.5, 130.1,
	128.5, 124.0, 120.1 (>C=), 37.9 (-SCH ₂ -), 37.1 (-SCH ₂ -), 27.9, 27.0,
	16.9, 13.6 (-CH ₃).
(3e)	$0.87, 9H (t, J = 8.0 Hz, -CH_3); 1.11 - 1.66, 18H (m, -CH_2-); 3.30, 4H$
	$(s, 2 \times -SCH_{2^{-}}); 6.39-7.39, 5H (m, Furyl-H + Ar-CH=CHCO).$
	186.2 (>C=O), 177.2 (-COO-), 170.7 (>C=), 152.2, 144.0, 127.6, 123.8,
	120.7, 114.4, 112.2 (>C=), 37.7 (-SCH ₂ -), 36.9 (-SCH ₂ -), 27.8, 27.0,
	$16.8, 13.6 (-CH_3).$

IR Spectra

It is well known that there are mainly three kinds of coordination types for trialkyltin carboxylates:^[16] the four-coordinate structure (A) for monomers, the intra-molecular five-coordinated structure (B) for monomers and the intermolecular five-coordinated structure (C) for polymers (see Figure 2).

The vacant 5d orbitals in a tin atom tend towards high coordination numbers with ligands containing lone electron pairs. IR stretching vibration frequencies of carbonyl groups in organotin carboxylates are important for determining their structures: when the structure changes from A to B or C, the asymmetric absorption vibration frequencies (υ asym) of carbonyl groups decrease and the symmetric absorption vibration frequencies (υ sym) increase.^[17] The difference [$\Delta \upsilon$ (C=O)], therefore, decreases.

From Table 2 we find that the Δv values of (3a)-(3e) are between 243–282 cm⁻¹, which suggests a possible tetrahedral structure (A) for them. However, in the region of 3384–3455 cm⁻¹, strong O—H stretching modes due to water molecules appeared. Hence, we believe that water coordination exists in (3a)-(3e) judging from their IR spectra. It should be noted that the structure reported here is quite different from the three kinds of coordination types in Figure 2.

NMR Spectra

¹H and ¹³C NMR spectra were recorded in chloroform-*d* as a solvent and the spectral assignments are given in Table 3. All Sn(IV) complexes explored here exhibited similar spectra.

In ¹H NMR spectra of (2), a singlet at *ca.* 3.4 ppm can be attributed to the protons of ethylenedithio groups. Two doublets which appear in the range of 6.6–7.7 and 7.5–7.8 ppm may be assigned to the vinylene protons with a three-bond coupling constant ${}^{3}J_{\rm H,H} = 16.0$ Hz. This is indicative of a *trans* carbon—carbon double bond. A broad peak of the carboxy proton is observed at 8.56 ppm for (**2a**) and 11.25 ppm for (**2d**).

In ¹H NMR spectra of (3), signals due to the protons of an α -oxoketene dithioacetal segment shift upfield compared to those of (2). For example,



Figure 2. The coordination types in trialkyltin carboxylates.



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	(3d)
Formula	$C_{52}H_{78}N_2O_{12}S_4Sn_2$
М	1288.69
Crystal system	Triclinic
Space group	ΡĪ
λ(Å)	0.71073
a (Å)	11.148(2)
b (Å)	16.656(3)
<i>c</i> (Å)	18.462(4)
α (°)	66.379(3)
β (°)	76.94(3)
γ (°)	87.95(3)
V (Å ³)	3053.6(11)
Ζ	2
Density (mg/mm ³)	1.389
$\mu (\mathrm{mm}^{-1})$	1.010
Crystal size (mm)	0.52 $ imes$ 0.42 $ imes$ 0.16
<i>T</i> (°C)	20(2)
Goodness-of-fit on F^2	0.923
R _{int}	0.0120
$R1 (I > 2\sigma(I))$	0.0566
WR2 (all data)	0.1644

Table 4. Crystallographic data for (3d).

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Table 5. Selected bond distance (\AA) and Angles $(^{\circ})$ for (3d).

Sn (1)-C (1)	2.11 (2)	C (9)-Sn (1)-C (5)	113.0 (10)
Sn (1)-O (1)	2.15 (3)	C (1)-Sn (1)-OW1	86.0 (10)
Sn (1)-C (9)	2.11 (2)	O (1)-Sn (1)-OW1	179.1 (7)
Sn (1)-C (5)	2.12 (2)	C (9)-Sn (1)-OW1	83.9 (10)
Sn (1)-OW1	2.49 (2)	C (5)-Sn (1)-OW1	87.8 (10)
Sn (2)-C (35)	2.09 (3)	C (35)-Sn (2)-C (31)	120.4 (12)
Sn (2)-C (31)	2.11 (2)	C (35)-Sn (2)-O (6)	94.9 (11)
Sn (2)-O (6)	2.20 (3)	C (31)-Sn (2)-O (6)	91.9 (10)
Sn (2)-C (27)	2.18 (3)	C (35)-Sn (2)-C (27)	125.2 (11)
Sn (2)-OW2	2.54 (2)	C (31)-Sn (2)-C (27)	112.8 (11)
C (1)-Sn (1)-O (1)	94.7 (10)	O (6)-Sn (2)-C (27)	95.4 (10)
C (1)-Sn (1)-C (9)	125.3 (10)	C (35)-Sn (2)-OW2	88.4 (11)
O (1)-Sn (1)-C (9)	96.2 (10)	C (31)-Sn (2)-OW2	85.6 (10)
C (1)-Sn (1)-C (5)	113.0 (10)	O (6)-Sn (2)-OW2	176.6 (6)
O (1)-Sn (1)-C (5)	91.2 (10)	C (27)-Sn (2)-OW2	83.6 (10)

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the protons of the ethylenedithio groups at *ca*. 3.4 ppm in free acids shift to *ca*. 3.3 ppm in tributyltin carboxylates. The protons of the methyl groups in the butyl groups are observed at *ca*. 0.8 ppm as triplets, while the protons of the methylene groups in the butyl groups are observed at 0.95-1.71 ppm as multiplets.

In ^{$\bar{1}3$}C NMR spectra, these complexes give signals at 185.7–186.6 ppm due to carbonyl carbon atoms and 176.4–180.3 ppm due to carboxy carbon atoms. The signals of the carbon atoms of benzene rings and vinylene are observed in the range of 112.2–170.7 ppm. The signals at 36.7–37.9 ppm are attributed to the carbon atoms of ethylenedithio groups. The signals due to the butyl groups are in the range of 13.4–27.9 ppm. The tin–carbon coupling peaks can be seen clearly. The coupling constants are ${}^{1}J_{119/117Sn-13C} = 680$ Hz and ${}^{2}J_{119/117Sn-13C} = 128$ Hz, respectively.



Figure 3. Molecular Structure of (3d).

Compound	Sn-O _{water} (Å)	Ref.
$PyCO_2Sn(CH_3)_3(H_2O)$	2.433	[18]
$(CH_3)_3Sn(NO_2)(H_2O)$	2.47	[19]
$PhSO_3Sn(CH_3)_3(H_2O)$	2.301	[20]
$4-NO_2-C_6H_4CH = CHCOC(C_3H_4S_2)$	2.492, 2.542	This work
$CO_2Sn(C_4H_9)_3(H_2O)$		

Table 6. Sn-O_{water} distances (Å) in aquatin(IV) complexes.

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Crystal Structure of (3d)

The crystallographic and experimental data for (3d) is listed in Table 4 and the selected bond sistance and angles for (3d) listed in Table 5. The crystal structure with numbering scheme of (3d) is shown in Figure 3. In the molecule each tin atom is coordinated to three carbon atoms of three butyl groups in an equatorial position and two oxygen atoms, one from a carboxylate group and the other from a water molecule, in an axial position, forming a distorted trigonal bipyramidal structure containing water of coordination. This is another proof of having a water molecule in the product. As listed in Table 3, $\angle C(1)Sn(1)C(5) + \angle C(5)Sn(1)C(9) +$ $\angle C(9)Sn(1)C(1) = 358.5^{\circ}$ which is nearly 360° . This indicates that the C(1), C(5), C(9) and Sn atoms are close to being coplanar. Two oxygen atoms occupy an axial position and the principal axis is almost linear with an O(1)-Sn(1)-OW(1) angle of 179.1°. The tin coordination environment slightly deviates from the ideal trigonal bipyramidal conformation.

In (**3d**), the bond lengths of Sn(1)–OW1 and Sn(2)–OW2 are 2.492 Å and 2.542 Å, respectively. The tin–water bond distance is only slightly larger than that in other aquatin(IV) complexes (Table 6).^[18–20]

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