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DI- AND TRIORGANOTIN(IV) DERIVATIVES OF 2-BENZOYLBENZOIC ACID *

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Summary

Six triorganotin(IV) 2-benzoylbenzoates, 2-$C_6H_5C(O)C_6H_4CO_2SnR_3$, where R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, c-C_6H_{11} and C_6H_5, two 2-benzoyl-3,4,5,6-tetrachlorobenzoates, 2-$C_6H_5C(O)C_6Cl_4CO_2SnR_3$, where R = CH_3 and C_6H_5 and two diorganotin(IV) bis-2-benzoylbenzoates, $[C_6H_5C(O)C_6H_4CO_2]_2SnR_2$, where R = CH_3 and C_6H_5, are prepared by metathesis between the organotin(IV) chloride and the sodium salt of the acid in ethanol, by azeotropically distilling water from benzene solutions of the bis-triorganotin(IV) oxide and the parent acid, or from a triorganotin(IV) hydroxide and the parent acid. The products are solids, and, except for the trimethyltin(IV) derivatives, are soluble in common organic solvents. Other Group IV ester derivatives of 2-benzoylbenzoic acid, 2-$C_6H_5C(O)C_6H_4CO_2MR_3$ (MR_3 = $Si(CH_3)_3$, $Ge(C_2H_5)_3$ and $Pb(C_6H_5)_3$), were also synthesized. ^{119m}Sn Mössbauer isomer shift (*IS*) values confirm the tin(IV) oxidation states and the quadrupole splittings (*QS*) (3.04–3.54 mm s^{-1}) and $\rho(QS/IS)$ values (2.16–2.70) specify higher than four-coordination at tin in the solid state. From the *QS* values of the diorganotin(IV) derivatives a point-charge model is used to calculate the carbon–tin–carbon angles. The magnitudes of these angles show that these derivatives adopt a *trans*-configuration in the solid, and that the triorganotin(IV) derivatives have equatorial-R_3Sn groups which are approximately planar. Absence of a ν_{asym}(Sn–C) mode in the infrared and a ν_{sym}(Sn–C) mode in the Raman specifies the planarity of the $(CH_3)_3Sn$ group in its solid derivative, but not in solution. Both bands appear for the $(CH_3)_2Sn$ derivative, ruling out a strictly linear array. The ketonic and carboxylate carbon–oxygen stretching frequencies are assinged at ca. 1650 and 1600 cm^{-1}, respectively, and it is concluded that the ketone group is not coordinated to the tin atom. The high values for the carbonyl stretching frequencies of the organosilyl- and germyl derivatives reflect four-coordination. NMR coupling constants, $|^2J(^{119}Sn-C-^1H)|$, reflect higher than four-coordination for the tri- and

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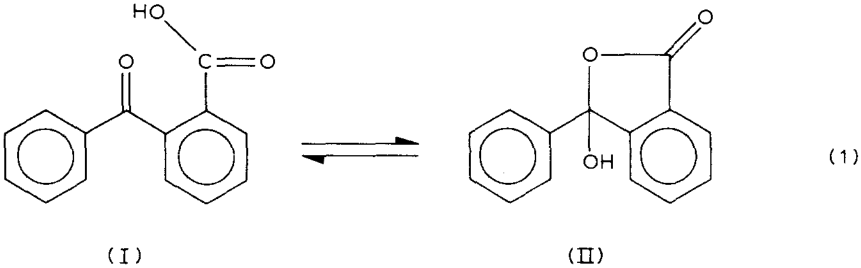
* Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June, 1983. J.J.Z. was a research student with Professor Emeléus at Sidney Sussex College in 1960–62, taking a Ph.D. in 1962.

dimethyltin(IV) derivatives in solution. ^{119}Sn NMR chemical shifts are to lower field than tetramethyltin for the aliphatic derivatives, reflecting low coordination, but not for the triphenyl- and diorganotin(IV) derivatives. Only one resonance is observed, so the open and lactol forms, if both are present, must be in rapid equilibrium. Carbon-13 resonances for the keto- and carboxylate carbons of the organotin derivatives resemble those of the open and not the lactol forms of the parent materials. No ditin or other fragments characteristic of the oligomer are seen in the mass spectrum at 70 eV. The evidence specifies an associated solid with bridging carboxylate groups from the open-form of 2-benzoylbenzoate in which the ketonic carbonyl group is not involved in coordination to the tin atom. The triorganotin(IV) derivatives contain equatorial-R_3Sn groups, and the diorganotin(IV) derivatives contain *trans*-R_2Sn groups.

Introduction

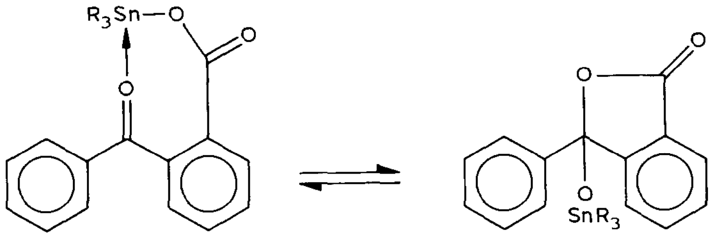
2-Benzoylbenzoic acid is an example of a non-enolizable carbonyl compound which exists in a ring-chain tautomeric equilibrium in solution. The relative amounts of the keto-acid (I) and the lactol (II) in solution can be varied depending upon the substitution pattern and the solvent polarity. For example, while the parent acid exists in the open form (I) in the solid state and dissolved in non-polar solvents, 2-benzoyl-3,4,5,6-tetrachlorobenzoic acid exists as the lactol (II) in the solid state and in very polar solvents [1]. Pseudo and normal esters can be formed from these tautomers, and infrared ν(C=O) frequencies can be used to distinguish the two forms (pseudo ester 1765, normal ester 1715 and 1663 cm^{-1}) [1,2].



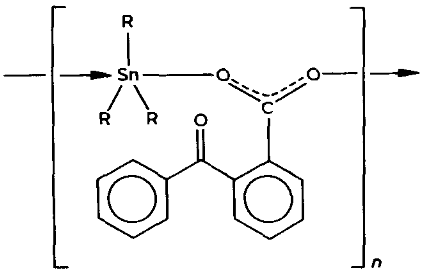
(1)

We have recently reported the synthesis of a series of organotin(IV) carboxylates in which the organic acid moiety contains a phosphine oxide substituent α- to the acetate [3]. These diphenylphosphinylacetate derivatives, $[(C_6H_5)_2P(O)CH_2CO_2)]_nSnR_{4-n}$ ($n = 1, 2$), contain tin atoms with coordination numbers greater than four, but it is the phosphinyl oxygen atom that binds in each case in preference to the more conventional carboxylate bridging [4]. Carboxylate bridging is also not the preferred form in the α-amino acid derivatives, $NH_2CHRCO_2SnR_3$, in which the amino nitrogen coordinates to the tin atom intermolecularly [5,6], but the triphenylphosphonopropionbetainetriorganotin(IV) salts, $[(C_6H_5)_3P(CH_2)_2CO_2SnR_3]^+$ X^-, are associated tin carboxylate linear polymers with dangling triphenylphosphonium cations [7].

We were thus particularly interested in preparing organotin(IV) esters of the 2-benzoylbenzoic acids. The product deriving from the open, keto-acid form (I), would be an organotin carboxylate ester with a ketonic carbonyl group in the γ-position potentially capable of intramolecularly coordinating to the tin atom to form a seven-membered heterocyclic system (III) or intermolecularly coordinating to form an associated, carboxylate-bridged polymer with dangling benzophenone groups (V). The product from the lactol form (II) would be an ester whose uncoordinated form (IV) is depicted in equilibrium with the monomeric carboxylate ester product (III). Both polymeric (VI) and monomeric coordinated forms are possible for the product from the lactol (II), but model studies favor the former, since the latter would necessitate rather severe distortions of the valence angles to produce the axial-carbonyl binding to the tin atom. The monomeric, intramolecularly-coordinated product (III) from the open-form would contain both axial- and equatorial-



(III) (IV) (2)



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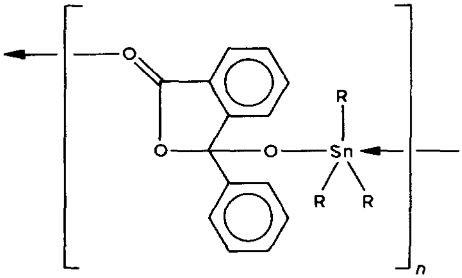

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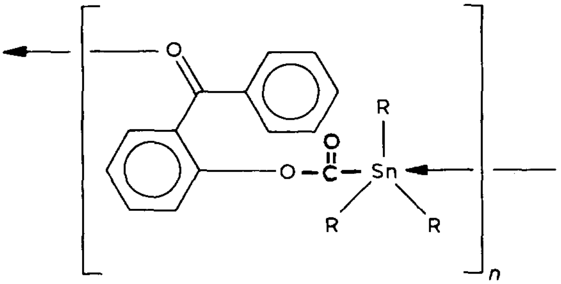

(VII)

oxygen atoms rather than the preferred axially-most-electronegative configuration with equatorial-triorganotin groups.

Ketones are generally weak donors toward tin, and isolable complexes usually involve the capacity for charge dispersal. However, we have recently solved the structure of the adduct of dimethyltin(IV) dichloride with diphenylcyclopropenone, $[(CH_3)_2SnCl_2 \cdot O{=}CC_2(C_6H_5)_2]_2$, which is a dimer in the solid state [8].

In this paper we report the synthesis and spectroscopic study of a series of di- and triorganotin(IV) 2-benzoylbenzoates. Di-n-butyltin bis-2-benzoylbenzoate has been claimed in a patent [9].

Experimental section

The starting organotin compounds were gifts from M&T Chemicals, Inc., and were used without further purification. 2-Benzoylbenzoic acid (Eastman) was recrystallized from ethanol or chloroform before use and 2-benzoyl-3,4,5,6-tetrachlorobenzoic acid was prepared from a Friedel–Crafts reaction between tetrachlorophthalic anhydride and benzene. The acid chloride of the latter acid, m.p. 183°C and the pseudo-methyl ester of 2-benzoylbenzoic acid, m.p. 90°C, were prepared by literature procedures [1]. Other reagents were articles of commerce.

The ^{119m}Sn Mössbauer spectra were recorded on a Ranger Engineering, constant-acceleration spectrometer equipped with an NaI scintillation counter. The source was $Ca^{119m}SnO_3$ (New England Nuclear Corp.) and $Ca^{119}SnO_3$ was the reference material for zero velocity at room temperature. The velocity calibration was based on β-tin and natural iron foils. The Ranger Engineering variable-temperature liquid nitrogen dewar and controller were regulated by a variable-bridge, silicon-controlled-rectifier circuit, and the measurements were done at 77 K. The data were stored in 512 channels of the Tracor Northern Model TN-1314 multichannel analyzer and the resultant spectra fitted using standard least-squares techniques assuming a Lorentzian shape.

Infrared spectra were recorded on a Beckman 4250 spectrometer as Nujol mulls on CsI discs, and the spectra were calibrated with polystyrene. Mass spectra were recorded on a Hewlett-Packard 5985B GC/MS system at 70 eV. ^{1}H and ^{13}C NMR data were obtained on Varian T-60 and IBM NR-80 instruments. The ^{119}Sn NMR spectra were recorded by M. Magerstädt at the Technical University of Berlin (Germany) on a Bruker SXP-109 instrument. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Raman spectra were recorded on a Spex Ramalog 5 spectrometer.

The compounds prepared, their microanalytical data, melting points and synthetic methods are listed in Table 1. The ^{119m}Sn Mössbauer parameters are found in Table 2, and the infrared data below 2000 cm^{-1} are found in Table 3. Table 4 compares the carbonyl stretching frequencies for various organometallic(IV) esters of 2-benzoylbenzoic acid. The ^{119}Sn NMR data are found in Table 5. Table 6 lists the ^{13}C NMR data for 2-benzoylbenzoic acid and selected organotin(IV) 2-benzoylbenzoates. Mass spectral data are listed in Table 7.

Trimethyltin(IV) 2-benzoylbenzoate, $2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(CH_3)_3$

To a solution of sodium (0.23 g, 10 mg-at) in ethanol (100 ml) was added 2-benzoylbenzoic acid (2.26 g, 10.0 mmol) followed by trimethyltin(IV) chloride

(1.99 g 10.0 mmol). The mixture was stirred for 1 h, and the precipitated sodium chloride was removed by filtration. The solvent was then evaporated, and the crude product was purified by reprecipitation from ethanol by ether. The compound melted sharply at 162–163°C, yield 80%.

Triethyltin(IV) 2-benzoylbenzoate, $2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_2H_5)_3$

To a solution of sodium (0.23 g, 10 mg-at) in ethanol (100 ml) was added 2-benzoylbenzoic acid (2.26 g, 10.0 mmol), and the sodium salt of the acid precipitated. To the suspension was added triethyltin(IV) chloride (2.41 g, 10.0 mmol) and the mixture was stirred for 1 h. The precipitated sodium chloride was filtered, and the solvent removed under vacuum. Ether was added to precipitate the product, m.p. 111–112°C, in 50% yield.

Tri-n-propyltin(IV) 2-benzoylbenzoate, $2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_3H_7\text{-}n)_3$

Bis-tri-n-propyltin(IV) oxide (2.56 g, 5.00 mmol) and 2-benzoylbenzoic acid (2.26 g, 10.0 mmol) were heated in benzene (a suspected carcinogen) for 2 h. The solvent

TABLE 1

DI- AND TRIORGANO-GROUP IV 2-BENZOYLBENZOATES

Compound	M.p. (°C)	Analyses (Found (calcd.) (%))		Yield (%)	Route
		C	H		
$2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(CH_3)_3$	162–163	52.10 (52.48)	4.83 (4.63)	80	1[a]
$2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_2H_5)_3$	111–112	54.52 (55.72)	5.57 (5.57)	50	1
$2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_3H_7\text{-n})_3$	49–50	58.41 (58.39)	6.59 (6.35)	100	2[b]
$2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_4H_9\text{-n})_3$	60–61	60.95 (60.62)	7.15 (6.99)	90	2
$2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_6H_{11}\text{-c})_3$	140–141	64.64 (64.79)	7.14 (7.09)	70	3[c]
$2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_6H_5)_3$	106–107	66.96 (66.70)	4.42 (4.17)	50	3
$2\text{-}C_6H_5C(O)C_6Cl_4CO_2Sn(CH_3)_3$	200–202(d)	38.40 (38.73)	3.05 (2.66)	50	1
$2\text{-}C_6H_5C(O)C_6Cl_4CO_2Sn(C_6H_5)_3$	55–59	54.14 (53.88)	3.07 (2.81)	70	1,3
$[2\text{-}C_6H_5C(O)C_6H_4CO_2]_2Sn(CH_3)_2$	178–180	59.93 (60.13)	4.34 (4.01)	80	4[d]
$[2\text{-}C_6H_5C(O)C_6H_4CO_2]_2Sn(C_6H_5)_2$	210–212	66.27 (66.42)	3.94 (3.87)	50	4
$2\text{-}C_6H_5C(O)C_6H_4CO_2Si(CH_3)_3$	–	68.69 (68.46)	6.01 (6.04)	100	5[e]
$2\text{-}C_6H_5C(O)C_6H_4CO_2Ge(C_2H_5)_3$	–	63.21 (62.40)	6.25 (6.24)	100	1
$2\text{-}C_6H_5C(O)C_6H_4CO_2Pb(C_6H_5)_3$	183–185	57.69 (57.90)	3.75 (3.62)	80	1

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[a] Triorganometal(IV) chloride + sodium salt. [b] Bis-triorganotin(IV) oxide + acid. [c] Triorganotin(IV) hydroxide + acid. [d] Diorganotin(IV) oxide + acid. [e] Hexamethyldisilazane + acid.

was then removed under vacuum to give a solid which was soluble in common organic solvents. This product was subjected to high vacuum for one day to remove traces of the organotin starting material. The yield was quantitative, m.p. 49–50°C.

Tri-n-butyltin(IV) 2-benzoylbenzoate, $2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_4H_9\text{-}n)_3$

Bis-tri-n-butyltin(IV) oxide (2.98 g, 10.0 mmol) and 2-benzoylbenzoic acid (2.26 g, 10.0 mmol) were reacted as before. The benzene was removed under vacuum to give 4.90 g of a cream-colored solid with a wide melting range. The pure product was obtained by heating under vacuum overnight, yield 90%, m.p. 60–61°C.

Tricyclohexyltin(IV) 2-benzoylbenzoate, $2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_6H_{11}\text{-}c)_3$

Tricyclohexyltin(IV) hydroxide (3.85 g, 10.0 mmol) and 2-benzoylbenzoic acid (2.26 g, 10.0 mmol) were refluxed in benzene in a Dean-Stark apparatus for 2 h. Then the solvent was removed on a rotary evaporator. Washing the resulting solid with ether gave the product in 70% yield, m.p. 140–141°C.

Triphenyltin(IV) 2-benzoylbenzoate, $2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_6H_5)_3$

Triphenyltin(IV) hydroxide (3.67 g, 10.0 mmol) and 2-benzoylbenzoic acid (2.26 g, 10.0 mmol) were heated in benzene in a Dean-Stark apparatus. The solvent was removed on a rotary evaporator, and traces of benzene were removed under vacuum. The crude product was recrystallized from ether to give the compound, m.p. 106–107°C, in 50% yield.

Trimethyltin(IV) 2-benzoyl-3,4,5,6-tetrachlorobenzoate, $2\text{-}C_6H_5C(O)C_6Cl_4CO_2\text{-}Sn(CH_3)_3$

To sodium (0.23 g, 10 mg-at) in absolute ethanol (100 ml) was added 2-benzoyl-3,4,5,6-tetrachlorobenzoic acid (3.64 g, 10.0 mmol). Sodium chloride precipitated immediately when solid trimethyltin(IV) chloride (1.99 g, 10.0 mmol) was then added. The mixture was refluxed for 1 h, cooled and the sodium chloride removed by filtration. The ethanol was evaporated and the last traces removed under vacuum. The title compound was recrystallized from ether in 50% yield. The compound shrinks at ca. 100°C before finally melting sharply at 200°C. The product can also be recrystallized from chloroform. The mass spectrum showed peaks at *m/e* (intensity) 512 (82.3) $[C_6H_5C(O)C_6Cl_4CO_2Sn(CH_3)_2]^{+\cdot}$; 467 (100) $[C_6H_5C(O)C_6Cl_4\text{-}Sn(CH_3)_2]^+$; 437 (23.9) $[C_6H_5C(O)C_6Cl_4Sn]^+$; 401 (9.2) $[CH{=}CHC(O)\text{-}C_6Cl_4SnCH_3]^+$; 165 (44.4) $[(CH_3)_3Sn]^+$; 155 (83.2) $[SnCl]^+$; 135 (58.2) $[CH_3Sn]^+$ and 120 $[Sn]^{+\cdot}$. At 12 eV, the only fragments are $[C_6H_5C(O)C_6\text{-}Cl_4CO_2Sn(CH_3)_2]^+$ (37.0) and $[C_6H_5C(O)C_6Cl_4Sn(CH_3)_2]^+$ (100).

Triphenyltin(IV) 2-benzoyl-3,4,5,6-tetrachlorobenzoate, $2\text{-}C_6H_5C(O)C_6Cl_4CO_2\text{-}Sn(C_6H_5)_3$

This compound was obtained in a similar manner from sodium (0.23 g, 10 mg-at), 2-benzoyl-3,4,5,6-tetrachlorobenzoic acid (3.64 g, 10.0 mmol) and triphenyltin(IV) chloride (3.85 g, 10.0 mmol) in 70% yield, m.p. 55–59°C. The same compound was obtained from the condensation between the acid (3.64 g, 10.0 mmol) and triphenyltin(IV) hydroxide (3.67 g, 10.0 mmol) in benzene. The mass spectrum showed peaks at *m/e* (intensity) 712 (2.6) $[C_6H_5C(O)C_6Cl_4CO_2Sn(C_6H_5)_3]^{+\cdot}$; 677 (5.9) $[C_6H_5\text{-}C(O)C_6Cl_4CO_2Sn(C_6H_5)_3 - Cl]^+$; 635 (32.0) $[C_6H_5C(O)C_6Cl_4CO_2Sn(C_6H_5)_2]^+$; 591

(35.4) $[C_6H_5C(O)C_6Cl_4Sn(C_6H_5)_2]^+$; 437 (16.8) $[C_6H_5C(O)C_6Cl_4Sn]^+$; 351 (22.4) $[(C_6H_5)_3Sn]^+$; 309 (32.4) $[(C_6H_5)_2SnCCH]^+$; 197 (67.7) $[C_6H_5Sn]^+$; 155 (64.8) $[SnCl]^+$ and 120 (43.9) $[Sn]^{+\cdot}$.

Attempted preparation of the pseudo ester isomer of triphenyltin(IV) 2-benzoyl-3,4,5,6-tetrachlorobenzoate, $\overline{OC(O)C_6Cl_4C_6H_5C}OSn(C_6H_5)_3$

Triphenyltin(IV) hydroxide (3.67 g, 10.0 mmol) and 2-benzoyl-3,4,5,6-tetrachlorobenzoic acid (3.64 g, 10.0 mmol) were refluxed for 1 h in nitromethane (100 ml). The solvent was then removed, and ether added. The cloudy solution was then filtered to remove undissolved solids, and the ether removed. The resulting solid, yield 90%, had an infrared spectrum identical with that of 2-$C_6H_5C(O)C_6Cl_4CO_2Sn(C_6H_5)_3$.

Dimethyltin(IV) bis-2-benzoylbenzoate, $[C_6H_5C(O)C_6H_4CO_2]_2Sn(CH_3)_2$

Dimethyltin(IV) oxide (1.66 g, 10.0 mmol) and 2-benzoylbenzoic acid (4.52 g, 20.0 mmol) were reacted in benzene as above. After refluxing for 2 h, the benzene was removed under vacuum. Ether was added to the resulting oil. The pure product was obtained by washing the precipitate with more ether, yield 80%, m.p. 178–180°C. The mass spectrum displayed peaks at m/e (intensity) values of 585 (31) $\{[C_6H_5C(O)C_6H_4CO_2]_2SnCH_3\}^+$; 541 (50) $\{[C_6H_5C(O)C_6H_4CO_2][C_6H_5C(O)C_6H_4]SnCH_3\}^+$; 497 (19.2) $\{[C_6H_5C(O)C_6H_4)]_2Sn\}^+$; 375 (45.2) $\{[C_6H_5C(O)\text{-}C_6H_4CO_2]Sn(CH_3)_2\}^+$; 331 (64.1) $[C_6H_5C(O)C_6H_4Sn(CH_3)]^+$; 301 (85.9) $[C_6H_5C(O)C_6H_4Sn]^+$; 135 (17.7) $[CH_3Sn]^+$; 120 (15.3) $[Sn]^{+\cdot}$ and 105 (100) $[C_6H_5CO]^+$. At 12 eV, the only fragments are $\{[C_6H_5C(O)C_6H_4CO_2]_2SnCH_3\}^+$ (84.6) and $\{[C_6H_5C(O)C_6H_4CO_2][C_6H_5C(O)C_6H_4]SnCH_3\}^+$ (100).

Diphenyltin(IV) 2-benzoylbenzoate, 2-$C_6H_5C(O)C_6H_4CO_2Sn(C_6H_5)_3$

Diphenyltin(IV) oxide (2.89 g, 10.0 mmol) and 2-benzoylbenzoic acid (4.52 g, 20.0 mmol) were heated in 150 ml benzene for 2 h. The benzene solution was filtered and then concentrated to a third of its original volume. The resulting precipitate was filtered and washed with ether to give the title compound in 50% yield, m.p. 210–212°C. The mass spectrum showed peaks at m/e (intensity) 647 (10.5) $\{[C_6H_5C(O)C_6H_4CO_2]_2SnC_6H_5\}^+$; 559 (5.1) $\{[C_6H_5C(O)C_6H_4CO_2][C_6H_5C(O)\text{-}C_6H_4]SnC_6H_5\}^+$; 499 (100) $[C_6H_5C(O)C_6H_4CO_2Sn(C_6H_5)_2]^+$; 455 (91.7) $[C_6H_5C(O)C_6H_4Sn(C_6H_5)_2]^+$; 301 (69.2) $[C_6H_5C(O)C_6H_4Sn]^+$; 197 $[C_6H_5Sn]^+$ and 120 (19.3) $[Sn]^{+\cdot}$.

Trimethylsilyl 2-benzoylbenzoate, 2-$C_6H_5C(O)C_6H_4CO_2Si(CH_3)_3$

Hexamethyldisilazane (1.61 g, 10.0 mmol) and 2-benzoylbenzoic acid (4.52 g, 20.0 mmol) were refluxed in a 1/1 mixture of benzene/hexane (150 ml) under a nitrogen atmosphere. The acid was only partly soluble in the hot solvent, but after 5 h, most of the solid had dissolved. Heating was continued for another 12 h, after which the solution was filtered hot to remove any insolubles. The solvent was then removed, and ether (100 ml) was added. The solution was again filtered, and the ether removed under vacuum. A cream-colored oil was obtained, $n_D^{25} = 1.5531$.

Triethylgermyl 2-benzoylbenzoate, 2-$C_6H_5C(O)C_6H_4CO_2Ge(C_2H_5)_3$

The sodium 2-benzoylbenzoate prepared from sodium (0.23 g, 10 mg-at) and 2-benzoylbenzoic acid (2.26 g, 10.0 mmol) was reacted with triethylchlorogermane

(1.95 g, 10.0 mmol) in ethanol. The sodium chloride was removed and the solvent evaporated. Traces of ethanol were removed under vacuum to give an oil which could not be crystallized; $n_D^{25} = 1.5615$.

Triphenyllead(IV) 2-benzoylbenzoate, $2\text{-}C_6H_5C(O)C_6H_4CO_2Pb(C_6H_5)_3$

In a similar manner, sodium (0.23 g, 10 mg-at), 2-benzoylbenzoic acid (2.26 g, 10.0 mmol) and triphenyllead(IV) chloride (4.74 g, 10.0 mmol) were reacted in ethanol to give the title compound in 80% yield, m.p. 183–185°C (d).

Sodium 2-benzoylbenzoate, $2\text{-}C_6H_5C(O)C_6H_4CO_2^-Na^+$

This salt was prepared from sodium metal (0.23 g, 10.0 mmol) and 2-benzoylbenzoic acid (2.26 g, 10.0 mmol) in ethanol (50 ml). Ether was added to the solid which was then filtered. The salt was washed with more ether and air-dried. It showed no signs of decomposition below 250°C. Yield 90%. The formulation of this compound was assumed.

Sodium 2-benzoyl-3,4,5,6-tetrachlorobenzoate, $2\text{-}C_6H_5C(O)C_6Cl_4CO_2^-Na^+$

This salt was prepared from sodium metal (0.23 g, 10.0 mmol) and 2-benzoyl-3,4,5,6-tetrachlorobenzoic acid (3.64 g, 10.0 mmol) in ethanol (50 ml). The solvent was removed and ether added. The white solid was collected by filtration and washed repeatedly with more ether, giving the compound in 90% yield, m.p. above 250°C. The formulation was also assumed.

Results and discussion

The synthesis of the triorganotin(IV) 2-benzoylbenzoates proceeds in good yield from the metathesis of the corresponding triorganotin(IV) chloride and the sodium salt of the acid in absolute ethanol, the reaction being driven to completion by the precipitation of sodium chloride (eq. 3):

$$R_3SnCl + 2\text{-}C_6H_5C(O)C_6H_4CO_2Na \rightarrow 2\text{-}C_6H_5C(O)C_6H_4CO_2SnR_3 + NaCl \qquad (3)$$
$$(R = CH_3, C_6H_5)$$

or from the reaction of the corresponding bis-triorganotin(IV) oxide with the parent acid, with the reaction driven to completion by the azeotropic distillation of the water released (eq. 4):

$$[R_3Sn]_2O + 2\ 2\text{-}C_6H_5C(O)C_6H_4CO_2H \rightarrow 2\ 2\text{-}C_6H_5C(O)C_6H_4CO_2SnR_3 + H_2O$$
$$(R = n\text{-}C_3H_7, n\text{-}C_4H_9) \qquad (4)$$

or from the analogous condensation reaction using the corresponding triorganotin(IV) hydroxide (eq. 5):

$$R_3SnOH + 2\text{-}C_6H_5C(O)C_6H_4CO_2H \rightarrow 2\text{-}C_6H_5C(O)C_6H_4CO_2SnR_3 + H_2O \qquad (5)$$
$$(R = c\text{-}C_6H_{11}, C_6H_5)$$

The diorganotin(IV) derivatives are synthesized in high yield from condensation reactions, starting from the diorganotin(IV) oxides in refluxing benzene (eq. 6):

$$R_2SnO + 2\ 2\text{-}C_6H_5C(O)C_6H_4CO_2H \rightarrow [2\text{-}C_6H_5C(O)C_6H_4CO_2]_2SnR_2 + H_2O \quad (6)$$
$$(R = CH_3, C_6H_5)$$

The other organometallic esters of 2-benzoylbenzoic acid were prepared by the sodium salt route (eq. 7):

$$R_3MCl + 2\text{-}C_6H_5C(O)C_6H_4CO_2Na \rightarrow 2\text{-}C_6H_5C(O)C_6H_4CO_2MR_3 + NaCl \qquad (7)$$

$$(MR_3 = Ge(C_2H_5)_3,\ Pb(C_6H_5)_3)$$

but the organosilyl compound was prepared by the condensation of hexamethyldisilazane with 2-benzoylbenzoic acid, in a method used for synthesizing trimethylsilyl carboxylates [10] (eq. 8):

$$(CH_3)_3SiNHSi(CH_3)_3 + 2\ 2\text{-}C_6H_5C(O)C_6H_4CO_2H \rightarrow$$

$$2\ 2\text{-}C_6H_5C(O)C_6H_4CO_2Si(CH_3)_3 + NH_3 \qquad (8)$$

Mössbauer data

The Mössbauer spectra for all the organotin compounds studied are well-resolved doublets whose isomer shifts (*IS*) specify tetravalent tin and whose quadrupole splittings (*QS*) and ρ (*QS*/*IS*) values (see Table 2) (3.04–3.54 and 2.16–2.70 mm s^{-1}, respectively) dictate higher than four-coordination at the tin atom [11]. Structure IV can thus be confidently ruled out. The failure of the trimethyl- and triphenyltin and dimethyl- and diphenyltin derivatives to give ambient temperature Mössbauer spectra argues against a highly associated polymeric lattice. The aliphatic compounds uniformly show a larger QS than the corresponding aromatic analogues.

For the dimethyl- and diphenyltin(IV) bis-2-benzoylbenzoates, we can apply the point-charge approximations to relate the observed *QS* to the carbon–tin–carbon angles [12]. These results correlate with the known X-ray data [4] for the dimethyl- [12–14] and diphenyltin(IV) [13] systems. Assuming that the partial quadrupole splitting of the ligand groups can be neglected, the carbon–tin–carbon angle in our dimethyltin compound is 154° and in the diphenyltin compound is 136°. These two derivatives hence adopt a distorted *trans*-R_2Sn geometry.

Triorganotin compounds with a trigonal bipyramidal geometry at the tin atom are known to have small quadrupole splittings if one of the three organic groups is at an apical position [15]. We assume that six-coordinated triorganotin compounds are not known [4], and since the *QS* values for the 2-benzoylbenzoates are in the range

TABLE 2

^{119m}Sn MÖSSBAUER DATA FOR THE DI- AND TRIORGANOTIN(IV) 2-BENZOYLBENZOATES IN mm s^{-1} AT 77 K

Compound	*IS* ± 0.03	*QS* ± 0.06	Γ_1 ± 0.03	Γ_2 ± 0.03	ρ (*QS*/*IS*)
$2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(CH_3)_3$	1.28	3.45	0.94	0.92	2.70
$2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_2H_5)_3$	1.47	3.51	1.06	1.04	2.39
$2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_3H_7\text{-n})_3$	1.46	3.54	1.23	1.25	2.42
$2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_4H_9\text{-n})_3$	1.46	3.50	0.99	0.95	2.40
$2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_6H_{11}\text{-c})_3$	1.55	3.46	1.05	1.01	2.24
$2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_6H_5)_3$	1.31	3.16	1.10	1.10	2.42
$2\text{-}C_6H_5C(O)C_6Cl_4CO_2Sn(CH_3)_3$	1.44	3.99	1.80	1.80	2.77
$2\text{-}C_6H_5C(O)C_6Cl_4CO_2Sn(C_6H_5)_3$	1.42	3.07	1.62	1.57	2.16
$[2\text{-}C_6H_5C(O)C_6H_4CO_2]_2Sn(CH_3)_2$	1.30	3.82	1.11	1.24	2.85
$[2\text{-}C_6H_5C(O)C_6H_4CO_2]_2Sn(C_6H_5)_2$	1.24	3.04	1.51	1.46	2.46

3.45–3.99 mm s^{-1} for the trialiphatic tin(IV) compounds and 3.07–3.16 mm s^{-1} for the triphenyltin(IV) derivatives, we conclude that the C_3Sn girdle is equatorial and rather flat in these systems.

Vibrational data

The stretching frequencies that are most important in these organotin derivatives are the ketonic C=O, the carboxyl CO_2 and the Sn–C bands. Table 3 lists the prominent bands for all the derivatives prepared.

In the ν(Sn–C) region, only one band is observed in the infrared for the 2-$C_6H_5C(O)C_6X_4CO_2Sn(CH_3)_3$ derivatives (X = H, Cl) at 546 cm^{-1}, and in the Raman spectrum only one band is seen at lower frequencies (X = H, 521; X = Cl, 519 cm^{-1}). We assign these absorptions in the infrared and Raman spectra to ν_{asym} and ν_{sym} (Sn–C), respectively, and conclude that the C_3Sn skeleton is planar in the solid state. In chloroform solution, however, a weak band is seen in the infrared at 511 cm^{-1}, thus ruling out strict planarity in this medium.

For the dimethyltin(IV) derivative, there are two weak bands in the ν(Sn–C) region at 574 and 542 cm^{-1} in the infrared and at 589w and 528vs cm^{-1} in the Raman spectrum. The observation of both ν_{asym} and ν_{sym}(Sn–C) rules out a strictly linear C_2Sn skeleton, and this conclusion is supported by calculations based upon Mössbauer *QS* data (vide supra). Bands at 575 and 555 cm^{-1} are seen in the infrared spectrum of a chloroform solution.

The normal methyl ester of 2-benzoylbenzoic acid exhibits two ν(C–O) bands, while the pseudo-ester of the lactol II exhibits only one [1,2]. However, there will be a severe lowering of the carboxylate stretching frequency owing to a mass effect if form I is adopted, in addition to any lowering of frequency arising from coordination to the tin atom as in forms III, V, VI and VIII. Thus it would be hazardous to use the position and number of these C–O stretching frequencies as a criterion for distinguishing between the ester and lactol configurations as well as whether coordination through the ketonic or carboxylate oxygens.

To assist the assignments, the 2-benzoylbenzoate derivatives 2-$C_6H_5C(O)C_6H_4$-CO_2MR_3 were synthesized where M = Si, Ge and Pb, and Table 4 compares the carbon–oxygen stretching frequencies. Trimethylsilyl acetate possesses a normal ester structure with the carbonyl stretching frequency at 1725 cm^{-1}. The $\nu_{asym}(CO_2)$ is found at 1635 cm^{-1} in trimethyltin(IV) alaninate which does not contain a coordinated carboxylate group, and at 1600 cm^{-1} in tricyclohexyltin(IV) alaninate which does [5]. The band at 1663 cm^{-1} in the normal ester, 2-$C_6H_5C(O)C_6H_4CO_2$-CH_3, would be expected to be shifted to lower energy in the corresponding organotin(IV) derivatives, whether by a mass effect or if the ketonic oxygen does engage in coordination. Thus the two sets of bands at ca. 1650 and 1600 cm^{-1} can be assigned to the ketonic and carboxylate stretching frequencies, respectively, in the organotin(IV) derivatives. Using this logic, the data in Table 4 can be rationalized. Triethylgermyl 2-benzoylbenzoate with bands at 1728 and 1617 cm^{-1} is a four-coordinated, normal ester. The bands at ca. 1650 in the organotin(IV) derivatives are relatively independent of the nature of the organic groups at tin. Coordination by a weakly basic ketonic oxygen would be expected to be sensitively affected by the steric bulk at tin. Thus we conclude that the ketonic oxygen is not coordinated to tin in these derivatives.

TABLE 3

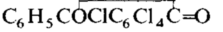
INFRARED DATA FOR THE DI- AND TRIORGANOMETALLIC(IV) 2-BENZOYLBENZOATES IN NUJOL FROM 2000 TO 400 cm^{-1}

2-$C_6H_5C(O)C_6H_4CO_2H$ [a]	1692sh, 1678vs, 1595w, 1574m, 1428m, 1312m, 1306m, 1292m, 1277m, 1257m, 933m, 767m, 701m
2-$C_6H_5C(O)C_6Cl_4CO_2H$ [b]	1755vs, 1372vs, 1280s, 1260s, 1227vs, 1149vs, 967s, 795s, 782s, 732s, 725vs, 695s, 670s, 590m,br, 505m
2-$C_6H_5C(O)C_6H_4CO_2Sn(CH_3)_3$ [c]	1652vs, 1639vs, 1629vs, 1610s, 1594vs, 1581s, 1570s, 1449s, 1342vs, 1315vs, 1288vs, 1255m, 1169m, 1145s, 936s, 928s, 850s, 814m, 799s, 774vs, 734s, 700s, 685s, 670s, 634m, 582m, 546s, 509m, 454s
2-$C_6H_5C(O)C_6H_4CO_2Sn(C_2H_5)_3$	1649vs, 1594s, 1578s, 1339vs, 1320vs, 1292vs, 1256s, 1149m, 1085m, 938m, 771s, 698m, 686m, 675s, 561w, 514m, 467m
2-$C_6H_5C(O)C_6H_4CO_2Sn(C_3H_7\text{-n})_3$	1660vs, 1652vs, 1595m, 1578m, 1332vs, 1282s, 1247m, 1143m, 1067m, 992m, 932m, 765s, 728s, 715s, 700s, 666m, 450w
2-$C_6H_5C(O)C_6H_4CO_2Sn(C_4H_9\text{-n})_3$	1664vs, 1597s, 1578s, 1336vs, 1279s, 1146m, 933m, 764s, 729m, 705vs, 671s, 450w
2-$C_6H_5C(O)C_6H_4CO_2Sn(C_6H_{11}\text{-c})_3$	1652s, 1639m, 1623m, 1595m, 1577w, 1365s, 1350s, 1314m, 1279m, 932m, 765m, 729m, 705m, 450w
2-$C_6H_5C(O)C_6H_4CO_2Sn(C_6H_5)_3$	1648vs, 1594s, 1576s, 1334vs, 1314s, 1276s, 1142m, 1077m, 933m, 763m, 729vs, 709s, 692vs, 556w, 440m
2-$C_6H_5C(O)C_6Cl_4CO_2Sn(CH_3)_3$ [d]	1679s, 1614vs, 1333vs, 1263vs, 985m, 780m, 762m, 683m, 652m, 586m, 546m
2-$C_6H_5C(O)C_6Cl_4CO_2Sn(C_6H_5)_3$	1677vs,br, 1598m, 1581m, 1482m, 1432vs, 1300vs,br, 1260vs, 1177m, 1130m, 1077m, 997m, 981m, 728vs, 695vs, 683s, 660s, 596m
[2-$C_6H_5C(O)C_6H_4CO_2]_2Sn(CH_3)_2$ [e]	1670s, 1663s, 1584s, 1578s, 1560m, 1540m, 1316m, 1284m, 934m, 798m, 766s, 729s, 700m, 686m, 679m, 574w, 542w, 450m
[2-$C_6H_5C(O)C_6H_4CO_2]_2Sn(C_6H_5)_2$ [f]	1677vs,br, 1598m, 1581m, 1482m, 1432vs, 1300vs,br, 1260vs, 1177m, 1130m, 1077m, 997m, 981m, 728vs, 695vs, 683s, 660s, 596m
2-$C_6H_5C(O)C_6H_4CO_2Si(CH_3)_3$ [g]	1775w, 1702vs, 1676vs, 1598s, 1582m, 1450s, 1302vs, 1255vs, 1135s, 1081m, 933s, 868s, 850vs, 830s, 765s, 732m, 730s, 710s, 696s, 660m, 630w
2-$C_6H_5C(O)C_6H_4CO_2Ge(C_2H_5)_3$ [g]	1728m, 1677vs, 1600s, 1584s, 1462sh, 1452s, 1315s,br, 1283sh, 1139s, 1084m, 1012m, 932s, 842m, 798m, 768s, 730s, 712s, 687s, 637m, 612m, 590m, 540w, 470w
2-$C_6H_5C(O)C_6H_4CO_2Pb(C_6H_5)_3$	1669s, 1660s, 1631m, 1614s, 1589s, 1560s, 1476s, 1450s, 1435m, 1431m, 1398s, 1345s, 1316s, 1296m, 1284s, 1250w, 1146m, 1016m, 984m, 937s, 844m, 769s, 737s, 729s, 725s, 715s, 696s, 683m, 670m, 440w

[a] In the sodium salt, $\nu(CO)$ 1668, $\nu_{asym}(CO_2)$ 1609, 1588 and $\nu_{sym}(CO_2)$ 1393 cm^{-1}. [b] In the sodium salt, $\nu(CO)$ 1674, $\nu_{asym}(CO_2)$ 1600 and $\nu_{sym}(CO_2)$ 1396 cm^{-1}. [c] In the Raman, $\nu_{asym}(Sn\text{–}C)$ 521 cm^{-1}. [d] In the Raman, $\nu_{asym}(Sn\text{–}C)$ 519 cm^{-1}. [e] In the Raman, $\nu_{asym}(Sn\text{–}C)$ 589, $\nu_{sym}(Sn\text{–}C)$ 528 cm^{-1}. These two bands are found at 575 and 555 cm^{-1} in the infrared of a chloroform solution. In hexachlorobutadiene, the CO and CO_2 bands are found at 1680m, 1665m, 1614vs cm^{-1}. [f] In hexachlorobutadiene, the CO and CO_2 bands are found at 1680m, 1636s and 1615vs cm^{-1}. [g] Neat liquid.

TABLE 4

COMPARISON OF THE CARBONYL STRETCHING FREQUENCIES OF THE 2-BENZOYLBENZOATE ESTERS $[2\text{-}C_6H_5C(O)C_6H_4CO_2]_{4\text{-}n}MR_n$ (n = 1, 2; M = C, Si, Ge, Sn, Pb) IN NUJOL

Ester	ν(CO) (cm^{-1})
$2\text{-}C_6H_5C(O)C_6H_4CO_2CH_3$ (normal-ester)[a]	1715, 1663
$2\text{-}C_6H_5C(O)C_6H_4CO_2CH_3$ (pseudo-ester)[a]	1765
$2\text{-}C_6H_5C(O)C_6H_4CO_2Si(CH_3)_3$	1702, 1676
$2\text{-}C_6H_5C(O)C_6H_4CO_2Ge(C_2H_5)_3$	1728, 1677
$2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_6H_5)_3$	1648, 1594, 1576
$2\text{-}C_6H_5C(O)C_6H_4CO_2Pb(C_6H_5)_3$	1669, 1660, 1631, 1614, 1589
 $C_6H_5COClC_6Cl_4C{=}O$	1785[b]
$[2\text{-}C_6H_5C(O)C_6H_4CO_2]_2Sn(CH_3)_2$	1670, 1663, 1584, 1578 1680[c], 1665[c], 1614[c]
$[2\text{-}C_6H_5C(O)C_6H_4CO_2]_2Sn(C_6H_5)_2$	1677, 1598, 1581 1680[c], 1636[c], 1615[c]

[a] Ref. 2. The band at 1715 cm^{-1} was assigned to the ester function, and the 1663 cm^{-1} band to the aromatic ketonic stretch. [b] Ref. 1. [c] In hexachlorobutadiene.

NMR data

The coupling constants, $|^2J(^{119}Sn\text{–}C\text{–}^1H)|$, for the trimethyltin(IV) derivatives, $2\text{-}C_6H_5C(O)C_6X_4CO_2Sn(CH_3)_3$, where X = H and Cl are 70.0 and 67.5 Hz, respectively. Thus the five coordinated structure persists in solution [16]. The coupling constant for the dimethyltin(IV) derivative is 82.0 Hz, also consistent with a higher than four-coordinated structure in solution, perhaps with a non-linear C_2Sn skeleton as predicted from the Mössbauer *QS* value (vide supra).

Raising the coordination number at tin moves the ^{119}Sn NMR chemical shift upfield of tetramethyltin, while substitution of electronegative groups moves the resonance downfield [16,17]. For the organotin(IV) 2-benzoylbenzoates, the tin chemical shift (see Table 5) is at lower field (positive values) than tetramethyltin for the aliphatic derivatives and to higher field (negative values) for the triphenyl- and both the diorganotin(IV) derivatives measured. Thus the higher coordination at the

TABLE 5

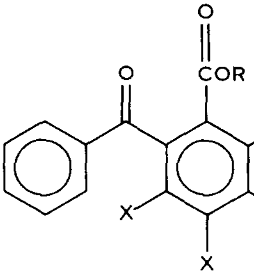
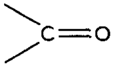
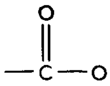
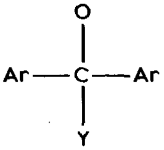
^{119}Sn NMR DATA FOR THE DI- AND TRIORGANOTIN(IV) 2-BENZOYLBENZOATES

Compound	δ[a] (ppm)
$2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(CH_3)_3$	33.8[b]
$2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_2H_5)_3$	125.1[b]
$3\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_3H_7\text{-n})_3$	125.5[b]
$2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_4H_9\text{-n})_3$	149.1[b]
$2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_6H_{11}\text{-c})_3$	29.8[b]
$2\text{-}C_6H_5C(O)C_6H_4CO_2Sn(C_6H_5)_3$	−97.8[b]
$2\text{-}C_6H_5C(O)C_6Cl_4CO_2Sn(CH_3)_3$	27.7[c]
$2\text{-}C_6H_5C(O)C_6Cl_4CO_2Sn(C_6H_5)_3$	−215.0[c]
$[2\text{-}C_6H_5C(O)C_6H_4CO_2]_2Sn(CH_3)_2$	−107.7[b]
$[2\text{-}C_6H_5C(O)C_6H_4CO_2]_2Sn(C_6H_5)_2$	−287.4[b]

[a] Relative to tetramethylstannane; positive values are to low field. [b] In $CDCl_3$. [c] In CD_3OD.

TABLE 6

^{13}C NMR DATA FOR 2-BENZOYLBENZOIC ACID AND SELECTED ORGANOTIN(IV) DERIVATIVES[a]

			C—Sn	
R = X = H	196	171	–	–
R = $(CH_3)_3Sn$; X = Cl[b]	194	169	−3	–
R = $(C_6H_{11}\text{-c})_3Sn$; X = H	197	170		
R = $(C_6H_5)_3Sn$; X = Cl	191	168	–	–
R = $(CH_3)_2Sn$; X = H	197	175	4	–
R = CH_3; X = H; Y = O (pseudo-ester)	–	168	–	109
$C_6H_5C\overline{OClC_6Cl_4C}{=}O$	–	162	–	99

[a] In ppm vs. tetramethylsilane in deuterochloroform-d_1. [b] In deuteromethanol-d_4.

tin atom in the diorganotin(IV) species indicated by the large Mössbauer *QS* values apparently persists in solution in accordance with the large NMR coupling constant of the dimethyl derivative measured in the same medium. Likewise, the triphenyltin(IV) compounds are also higher coordinated in solution. However, three of the trialkyltin(IV) derivatives which contain methyl and cyclohexyl groups also have rather low positive shifts, near that of tetramethyltin(IV). The coupling constant data for the two trimethyl derivatives indicate five-coordination in solution, and we believe that the tin chemical shift values are corroboratory for all three species being at least partially associated. The large low field shifts for the longer straight chain aliphatic species indicate monomeric, four-coordinated structures in solution. In all cases only one resonance is observed. Thus if both normal ester and lactol forms exist, they must be interconverting rapidly with respect to the NMR time scale through equilibria such as that depicted in eq. 2.

In the parent 2-benzoylbenzoic acid the ^{13}C NMR (see Table 6) of the ketonic carbon is found at 196 ppm, while that of the carboxylate carbon is at 171 ppm relative to tetramethylsilane. The lactone from the acid chloride of the tetrachloro derivative, on the other hand, exhibits a resonance at 162 for the carboxylate carbon, but the ketal carbon now appears at 99 ppm. The carboxylate carbon of the methyl ester of the lactol II resonates at 168 ppm and the ketal carbon at 109 ppm. The data for four of the organotin(IV) derivatives sufficiently soluble for study are close to those for the open-form and not the lactol, thus ruling out the lactol forms IV and VI for our products. The resonances of the carboxylate carbons in the tetrachloro and the pseudo-ester derivatives are found at somewhat lower field.

TABLE 7

MASS SPECTRAL DATA FOR THE TRIORGANOTIN(IV) 2-BENZOYLBENZOATES AT 70 eV[a]

R	$[C_6H_5C(O)C_6H_4CO_2SnR_3]^{+\cdot}$	$[C_6H_5C(O)C_6H_4CO_2SnR_2]^+$	$[C_6H_5C(O)C_6H_4SnR_2]^+$	$[C_6H_5C(O)C_6H_4Sn]^+$	$[R_3Sn]^+$	$[R_2Sn]^+$	$[RSn]^+$	$[Sn]^{+\cdot}$
CH_3	–	61.4 (100[b])	69.9 (35.0[b])	51.1	100[c]	23.2[c]	–	37.3
C_2H_5	–	100	68.4	96.8	–	–	19.3	29.4
n-C_3H_7	–	100	26.9	63.4	–	–	17.9	30.7
n-C_4H_9	–	100	20.1	60.8	–	–	26.9	28.1[d]
c-C_6H_{11}	–	100	52.2[e]	62.8	–	–	–	7.7[d]
C_6H_5[b]	62.6	100	5.1	–	19.4	21.1	–	7.7

[a] Based upon masses ^1H, ^{12}C, ^{16}O and ^{120}Sn. [b] Recorded at 12 eV. [c] Peaks overlapped. [d] $[HSn]^{+\cdot}$. [e] $[C_6H_5C(O)C_6H_4SnH_2]^+$.

Mass spectral data

For the triorganotin(IV) derivatives (see Table 7) a parent molecular ion is only seen for the triphenyl derivative, but no fragments higher than the parent and no ditin or other combinations of atoms which would arise from oligomers are seen. The most intense peak, except in the trimethyltin case, is the fragment $[C_6H_5C(O)C_6H_4CO_2SnR_2]^+$, which subsequently loses a molecule of carbon dioxide. Heating the compounds themselves, however, fails to liberate CO_2. For the trimethyl derivative, the base peak at 70 eV is the $[(CH_3)_3Sn]^+$ fragment, and the $[C_6H_5C(O)C_6H_4CO_2Sn(CH_3)_2]^+$ ion is also found in high abundance. The latter ion is the base peak at 12 eV.

The mass spectrum of the parent, 2-benzoylbenzoic acid (I), which exists in the open form in the solid state [18], is different from that of the tetrachloro derivative which may be in the lactol form (II) in the solid. The prominent fragments for I are: $[M - C_6H_5]^+$ (43.4%), $[M - CO_2H]^+$ (26.4%) and $[C_6H_5CO]^+$ (100%) (M = molecular ion) and for the tetrachloro derivative are: $M^{+\cdot}$ (39.8%), $[M - CO_2H]^+$ (11.6%) $[C_6Cl_4C(O)C_2H_2OH]^+$ (75.5%) and $[C_6H_5CO]^+$ (100%) (M = molecular ion).

Structural conclusions

From the Mössbauer *QS* data the tin atoms are all higher than four-coordinated and this is corroborated by $|^2J(^{119}Sn-C-^1H)|$ values in the ^1H NMR and ^{119}Sn chemical shifts. From ^{13}C NMR chemical shift evidence the open form and not the lactol is the one adopted. From vibrational stretching frequencies for the carbon–oxygen bonds, the ketonic carbonyl group is not involved in coordination to the tin atom. This combination of evidence rules out forms III, IV, VI and VII, leaving only the carboxylate-bridged V, containing equatorial R_3Sn groups. Presumably, the corresponding six-coordinated, *trans*-R_2Sn octahedral form is adopted by the diorganotin(IV) derivatives.

This conclusion is supported by the structure of bis(2-benzoylbenzoato)-copper(II)-4-iodoaniline which contains open-form 2-benzoylbenzoato moieties which act as bidentate bridging ligands. The ketonic carbonyl groups are not involved in coordinating to the copper center [19].

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