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SYNTHESIS OF TRIPHENYLPHOSPHONOPROPIONBETAINETRIORGANOTIN(IV) SALTS $[(C_6H_5)_3P(CH_2)_2CO_2SnR_3]^+ X^-$, BY NUCLEOPHILIC DISPLACEMENT OF ANIONS FROM TRIORGANOTINS

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Summary

Trimethyl- and triphenyl-tin(IV) hydroxide act on triphenyl(2-carboxyethyl)-phosphonium hydrochloride, which is made from 3-chloropropionic acid and triphenylphosphine, to release water in the presence of dimethylformamide (DMF) as a catalyst. The water is azeotropically distilled to drive the reaction forward and produce triphenylphosphonopropionbetainetrimethyl- and triphenyl-tin(IV) chlorides in high yield. The latter product also results from the displacement of chloride from triphenyltin(IV) chloride by the phosphobetaine, $(C_6H_5)_3P(CH_2)_2CO_2$, which is made by treating the phosphonium hydrochloride with bicarbonate, and the compounds $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ X^-$ where X = Cl, Br, I, N_3, NCS, NO_3, $B(C_6H_5)_4$ and $Co(CO)_4$ are made in the same way. The acetate salt results from metathesis from the chloride and lead(II) acetate. A double salt, $[(C_6H_5)_3P(CH_2)_2CO_2SnR_3]^+ [R_3SnX_2]^-$, is formed for X = Cl, Br and N_3 by adding additional $(C_6H_5)_3SnX$ to the already-formed simple salts. Double salts are also obtained from the 1/1 reactions between the phosphobetaine and triphenyltin(IV) isocyanate and methyldiphenyltin(IV) chloride. The phosphonium chloride double salt could be converted to the thiophosphonium derivative by heating with elemental sulfur in ethanol. The products of these novel nucleophilic displacement reactions are high melting solids. Tin-119m Mössbauer data are consistent with five-coordinated, triorganotin(IV) formulations with the exception of the diphenyl(8-hydroxyquinolinato)tin(IV) chloride salt in which the tin atom is six-coordinated, and the diphenyltin system *cis*-oriented. The parameters otherwise do not change with the nature of the X group, which in the tetracarbonylcobaltate derivative is tetrahedral by infrared, establishing the ionicity of the products. The chloride exhibits a molar conductivity indicative of a 1/1 electrolyte in DMF. A bridging acetate structure in the solid is consistent with the lowered $\nu(CO_2)$ frequencies. The Mössbauer spectra of the double salts give simple doublets of lowered isomer shift (IS) and raised quadrupole splitting (QS) which may arise from a cross-linking ion pairing of the polymer chains in the solid, and the NMR spectra of the two methyltin derivatives shows only a single resonance line and tin satellites which is rationalized by a dynamic exchange process. The products are formulated as associated tin carboxylate polymers with dangling triphenylphosphonium cations.

Triorganotin compounds R_3SnX are of commercial interest as biocidal materials, but the nature of the X group does not have a marked effect on the biological activity [1]. Organophosphorus compounds also exhibit strong biocidal activity [2], and it may be possible to confer desirable biocidal characteristics on the triorganotin compound by incorporating an organophosphorus substituent on the X group.

Following our previous work on the tin amino acids [3—6], we looked for a carboxylic acid with an organophosphorus substituent. There has been considerable interest in the structures of the triorganotin carboxylates [7], and five-coordinated, one-dimensional polymeric structures with the more electronegative oxygen groups in the axial-positions have been confirmed by X-ray studies [7—11]. Of the organophosphorus compounds, the tetraorganophosphonium salts are known to behave as phase-transfer catalysts, and they have the ability to alter the surface tension of water [12]. We, therefore, decided to prepare triorganotin derivatives of triphenyl(2-carboxyethyl)phosphonium chloride, $[(C_6H_5)_3P(CH_2)_2CO_2H]^+ Cl^-$, to test the effect of this novel group.

Experimental

The phosphonium cation, triphenyl(2-carboxyethyl)phosphonium, is easily prepared in high yield from the reaction of 3-chloropropionic acid and triphenylphosphine. The triphenylphosphonopropionbetaine is derived in high yield from the product by treatment with sodium bicarbonate in ethanol [13]. Triphenyltin(IV) chloride and triphenylphosphine were gifts from M & T Chemicals, Inc., and 3-chloropropionic acid was from the Aldrich Chemical Co. Other organotin derivatives were prepared from the reaction between triphenyltin(IV) chloride and the potassium salt of the halide or pseudohalide in ethanol. In this way, we prepared triphenyltin(IV) bromide, m.p. 115—116°C (lit. 120—121°C [14], 121.5—122.5°C [15]), triphenyltin(IV) iodide, m.p. 120—121°C (lit. 122—124°C [16]), triphenyltin(IV) isothiocyanate, m.p. 166—168°C (lit. 166—168°C [17], 171—172°C [18]), triphenyltin(IV) isocyanate, m.p. 98—100°C (lit. 98—99°C [19]) and triphenyltin(IV) azide, m.p. 114°C (lit 117°C [20]). Methyldiphenyltin(IV) chloride was prepared from the cleavage of methyltriphenyltin by elemental iodine in chloroform [21].

Diphenyltin(IV) chlorooxinate was prepared from 8-hydroxyquinoline and diphenyltin(IV) dichloride, m.p. 164—165°C (lit. 167—168°C [22,23]).

Triphenyltin(IV) nitrate [24] was prepared and reacted in situ, as was triphenyltin(IV) tetraphenylborate [25,26]. Triphenyltin(IV) tetracarbonylcobaltate was prepared by the reaction of triphenyltin(IV) chloride and sodium tetracarbonylcobaltate from the sodium metal cleavage of octacarbonyldicobalt [27].

The ^{119m}Sn Mössbauer spectra were recorded on a Ranger Engineering constant acceleration spectrometer equipped with a sodium iodide scintillation counter. The source was $Ca^{119m}SnO_3$ (New England Nuclear Corp.) and $Ca^{119m}SnO_3$ was the reference material for zero velocity at room temperature. The velocity calibration was based on β-tin and natural iron. The Ranger Engineering variable-temperature was kept at 77 K for the measurements. The data were stored in 512 channels of the Tracor Northern Model TN-1314 multichannel analyzer and the resultant spectra fitted assuming a Lorentzian line shape.

Infrared spectra were recorded on a Beckman 4250 spectrometer as Nujol mulls, and the spectra were calibrated with polystyrene. Proton magnetic resonance spectra were recorded at room temperature at a sweep width of 500 Hz in deuterated chloroform with tetramethylsilane as the internal standard on Varian T-60 spectrometer. Raman data were recorded on a Spex Ramalog 5 laser spectrometer. Conductivity was measured on an Industrial Instruments Conductivity Bridge Model RC-16B2.

Carbon and hydrogen analyses were carried out by Galbraith Laboratories Inc., Knoxville, Tennessee. Melting points were determined on a Thomas—Hoover capillary melting point apparatus and are listed uncorrected.

Triphenylphosphonopropionbetainetrimethyltin(IV) chloride, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(CH_3)_3]^+ Cl^-$. Trimethyltin(IV) hydroxide (1.81 g, 10.0 mmol) and triphenyl(2-carboxyethyl)phosphonium chloride (3.71 g, 10.0 mmol) were dissolved in dry benzene (a suspected carcinogen) (150 ml) and dimethylformamide (7 ml) and heated for 30 min in a Dean-Stark assembly to remove the water formed. The benzene was removed on a rotary evaporator and the pure compound obtained in 80% yield m.p. 173—174° C, by recrystallization from 2-propanol.

Triphenylphosphonopropionbetainetriphenyltin(IV) chloride, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ Cl^-$. Triphenyltin(IV) hydroxide (3.67 g, 10.0 mmol) and triphenyl(2-carboxyethyl)phosphonium chloride (3.71 g, 10.0 mmol) were combined in dry benzene (150 ml) and dimethylformamide (7 ml). The benzene suspension was heated with magnetic stirring in a flask equipped with a Dean-Stark trap, and the theoretical amount of water was collected in ten minutes. The white precipitate was collected by suction filtration, washed with ethanol and then with ether and air-dried to give the title compound, m.p. 195—197° C, in 90% yield.

This same compound was also prepared by mixing warm ethanolic solutions of the phosphonium betaine, $(C_6H_5)_3P^+(CH_2)_2CO_2^-$ (3.34 g, 10.0 mmol), and triphenyltin(IV) chloride (3.85 g, 10.0 mmol). The white precipitate formed on cooling, was filtered, washed with ethanol and then ether; m.p. 194—195° C, yield 70%. The melting point of an intimate mixture of the two products is not depressed, and their infrared spectra are identical.

The corresponding bromide and iodide salts were prepared by the second method, and their melting points and yields are listed in Table 1.

Triphenylphosphonopropionbetainetriphenyltin(IV) isothiocyanate $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ NCS^-$. Mixing triphenyltin(IV) isothiocyanate (2.04 g, 5.00 mmol) and the phosphonobetaine, $(C_6H_5)_3P^+(CH_2)_2CO_2^-$ (1.67 g, 5.00 mmol), in ethanol (50 ml) gave an immediate precipitate, m.p. 198—199° C, in 90% yield. When the amount of the organotin was doubled, the product obtained after washing with ethanol had an identical melting point and infrared spectrum.

Triphenylphosphonopropionbetainetriphenyltin(IV) acetate, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ CH_3CO_2^-$. Triphenylphosphonopropionbetainetriphenyltin chloride (2.88 g, 4.00 mmol) and lead acetate trihydrate, $Pb(CH_3CO_2)_2 \cdot 3H_2O$ (0.76 g, 2.0 mmol) were allowed to react in hot ethanol (50 ml) to give lead(II) chloride which precipitated immediately and was removed by filtration. The resulting solution was concentrated to give the product, m.p. 170—173° C, in 50% yield.

Triphenylphosphonopropionbetainetriphenyltin(IV) nitrate, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ NO_3^-$. A solution of triphenyltin chloride (3.85 g, 10.0 mmol) in acetone (50 ml) was added to a solution of silver nitrate (1.70 g, 10.0 mmol) in water (5 ml). The silver chloride which precipitated immediately was filtered. To this solution of triphenyltin(IV) nitrate was added the phosphonium betaine, $(C_6H_5)_3P^+(CH_2)_2CO_2^-$ (3.34 g, 10.0 mmol) in ethanol (10 ml), the solution concentrated and ether added to precipitate the white product, which was recrystallized from acetone, m.p. 162—164° C, in 80% yield.

Triphenylphosphonopropionbetainetriphenyltin(IV) tetraphenylborate, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ B(C_6H_5)_4^-$. Triphenyltin(IV) chloride (3.85 g, 10.0 mmol) and sodium tetraphenylborate (3.42 g, 10.0 mmol) were mixed in 2-propanol (50 ml). The resulting sodium chloride was filtered, and the solution was mixed with the phosphonium betaine, $(C_6H_5)_3P^+(CH_2)_2CO_2^-$ (3.34 g, 10.0 mmol) in 2-propanol (50 ml) to precipitate the white product, m.p. 190—192° C, in 60% yield, which was washed with ethanol and ether.

Triphenylphosphonopropionbetainetriphenyltin(IV) tetracarbonylcobaltate(I) $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [Co(CO)_4]^-$. Triphenyltin(IV) tetracarbonylcobaltate(I) [27] (2.60 g, 5.00 mmol) was dissolved in acetone (20 ml) and mixed with the betaine (1.67 g, 5.00 mmol) dissolved in ethanol (20 ml). No precipitate formed immediately but a brown solid formed on slow evaporation of the solvent. This was filtered and recrystallized from acetone, m.p. 107—108° C, in 60% yield.

Triphenylphosphonopropionbetainetriphenyltin(IV) triphenyltin(IV) dichloride, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3SnCl_2]^-$. Triphenyltin(IV) chloride (3.85 g, 10.0 mmol) and $(C_6H_5)_3P^+(CH_2)_2CO_2^-$ (1.67 g, 5.00 mmol) were each dissolved in hot ethanol (20 ml) and then mixed. On slowly cooling the mixture, a white semi-solid was obtained. Triturating this in hot ethanol gave a precipitate, m.p. 188—190° C, which was filtered and washed with ethanol and then ether, to give the double salt in 80% yield.

Triphenylphosphonopropionbetainetriphenyltin(IV) triphenyltin(IV) dibromide, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3SnBr_2]^-$. A similar procedure with triphenyltin(IV) bromide gave the product in 60% yield, m.p. 184—185° C.

Triphenylphosphonopropionbetainetriphenyltin(IV) triphenyltin(IV) diisocyanate, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3Sn(NCO)_2]^-$. Triphenyltin(IV) isocyanate (3.92 g, 10.0 mmol) reacted with triphenylphosphonopropionbetaine (3.34 g, 10.0 mmol) in ethanol (50 ml), to form the 1/2 product in 60% yield, m.p. 149—152° C.

Triphenylphosphonopropionbetainetriphenyltin(IV) triphenyltin(IV) diazide, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3Sn(N_3)_2]^-$. A semi-solid which formed immediately on mixing the phosphorus betaine (1.67 g, 5.00 mmol) and triphenyltin(IV) azide (3.92 g, 10.0 mmol) in ethanol became a powder on trituration and warming, m.p. 152—153°C, yield 80%.

Triphenylphosphonopropionbetainemethyldiphenyltin(IV) methyldiphenyltin(IV) dichloride, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(CH_3)(C_6H_5)_2]^+$ $[(CH_3)(C_6H_5)_2SnCl_2]^-$. Methyldiphenyltin(IV) chloride (3.23 g, 10.0 mmol) was added dropwise to an ethanolic solution of triphenylphosphonopropionbetaine (3.34 g, 10.0 mmol) and the solution concentrated to precipitate a solid which was recrystallized from chloroform. Instead of the anticipated 1/1 product, the compound isolated analyzed as the above formulation, m.p. 105—106°C, in 30% yield.

Triphenylphosphonopropionbetainediphenyltin(IV) 8-hydroxyquinolinatochloride, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_2(C_9H_6NO)]^+$ Cl^-. The betaine (0.84 g, 2.5 mmol) dissolved in ethanol (20 ml) and diphenyltin(IV) chlorooxinate (1.13 g, 2.50 mmol) dissolved in a benzene/ethanol mixture were mixed. Slow evaporation of the solvent mixture yielded the yellow product, m.p. 172—175°C, in 30% yield.

Triphenylthiophosphonopropionbetainetriphenyltin(IV) triphenyltin(IV) dichloride, $[(C_6H_5)_3PS(CH_2)_2CO_2Sn(C_6H_5)_3]^+$ $[(C_6H_5)_3SnCl_2]^-$. Triphenylphosphonopropionbetainetriphenyltin(IV) chloride (3.60 g, 5.00 mmol) was dissolved in boiling ethanol (150 ml) and elemental sulfur (0.16 g, 5.0 mg-at) added. The sulfur dissolved completely on stirring. A cream-colored precipitate which melted to a red liquid at 174—175°C formed on cooling.

Attempted dehydrochlorination of triphenylphosphonopropionbetainetriphenyltin(IV) chloride

A suspension of sodium hydride in mineral oil (57% suspension, 0.42 g, 10 mmol) was washed with petroleum ether and dissolved in dimethylsulfoxide [28]. Triphenylphosphonopropionbetainetriphenyltin(IV) chloride (7.19 g, 10.0 mmol) in DMSO was added and the mixture stirred for 30 min. The solution was then added to water and the precipitate, m.p. 191—192°C was collected and recrystallized from ethanol. The product was identified through carbon and hydrogen analysis, melting point, infrared and mass spectroscopy to be $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+$ $[(C_6H_5)_3SnCl_2]^-$.

The compounds prepared, along with their m.p.'s, yields and microanalytical data are listed in Table 1. Difficulty was experienced in obtaining correct microanalytical data for carbon on compounds 3, 4, 6—10, 12, 14, 16 and 17 and for hydrogen on compounds 3, 4, 14 and 17 listed in Table 1. The tin-119m Mössbauer data are gathered in Table 2, and the infrared data in Table 3.

Results and discussion

The action of triphenyltin(IV) hydroxide on triphenyl(2-carboxyethyl)phosphonium hydrochloride in benzene releases water and gives the triorganotin carboxylate in ca. 90% yield after heating in a Dean-Stark apparatus for ten minutes with dimethylformamide (DMF) as a catalyst:

$$[(C_6H_5)_3P(CH_2)_2CO_2H]^+Cl^- + (C_6H_5)_3SnOH \xrightarrow{DMF} [(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+Cl^- + H_2O \quad (1)$$

TABLE 1

TRIPHENYLPHOSPHONOPROPIONBETAINEORGANOTIN(IV) SALTS

Compound	Mp (°C) (decomp.)	Analysis (Found (calcd.) (%))		Yield (%)
		C	H	
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(CH_3)_3]^+ Cl^-$	173–174	54,19(54.01)	5,31(5.25)	80
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ Cl^-$	195–197	65,09(65.07)	4,79(4.73)	90
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ Br^-$	183–184	62,01(61.29)	4,59(4.45)	80
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ I^-$	183–184	60,58(57.74)	4,61(4.19)	70
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ NCS^-$	198–199	64,81(64.72)	4,64(4.58)	90
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ N_3^-$	154–155	62,79(64.49)	4,63(4.69)	70
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ NO_3^-$	162–164	61,39(62.76)	4,70(4.46)	80
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ CH_3CO_2^-$	170–173	64,55(66.24)	4,90(4.98)	50
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ B(C_6H_5)_4^-$	190–192	71,94(75.41)	5,45(5.39)	60
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ Co(CO)_4^-$	107–108	56,35(60.38)	4,58(4.33)	60
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3SnCl_2]^-$	188–190	61,66(61.93)	4,53(4.44)	80
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3SnBr_2]^-$	183–184	59,44(57.32)	4,48(4.11)	60
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3Sn(N_3)_2]^-$	152–153	61,36(61.21)	4,59(4.39)	80
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3Sn(NCO)_2]^-$	149–152	61,22(63.36)	4,80(4.39)	60
$[(C_6H_5)_3P(CH_2)_2CO_2SnCH_3(C_6H_5)_2]^+ [CH_3(C_6H_5)_2SnCl_2]^-$	105–106	57,60(57.52)	4,95(4.59)	30
$[(C_6H_5)_3PS(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3SnCl_2]^-$	173–174	58,13(60.19)	4,30(4.31)	50
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_2(C_9H_6NO)]^+ Cl^-$	172–175	62,89(64.11)	4,07(4.45)	30

The same tin product results from the displacement of chloride by the phosphobetaine, $(C_6H_5)_3P^+(CH_2)CO_2^-$:

$$(C_6H_5)_3P^+(CH_2)_2CO_2^- + (C_6H_5)_3SnCl \rightarrow [(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+Cl^- \quad (2)$$

Other organotin carboxylates with an organophosphorus substituent are prepared by this novel nucleophilic displacement of the chloride or pseudohalide from the triorganotin(IV) moiety.

There has been controversy over the structure of the $(C_6H_5)_3P^+(CH_2)_2CO_2^-$ moiety which we call triphenylphosphonopropionbetaine in accordance with recommended nomenclature [29,30]; but as has been pointed out, phosphorus-31 NMR measurements fail to differentiate between the phosphobetaine structure, A, and the ylid structure, B [31]:

$$\underset{(A)}{(C_6H_5)_3P^+(CH_2)_2CO_2^-} \qquad \underset{(B)}{(C_6H_5)_3P{=}CHCH_2CO_2H \leftrightarrow (C_6H_5)_3P^+\,\bar{C}HCH_2CO_2H}$$

Our results indicate that the correct form is probably structure A which would lead to the formation of tin—oxygen bonds, whereas B would be expected to lead to the formation of tin—carbon bonds. The latter products would be easily identified by tin-119m Mössbauer spectroscopy, since because the tin atom is surrounded by four organic groups, simple singlet spectra with no quadrupole splitting (QS) would be expected [32].

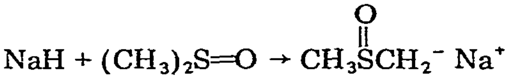
The phosphonium hydrochloride, $[(C_6H_5)_3P(CH_2)_2CO_2H]^+Cl^-$, is prepared by reacting triphenylphosphine with 3-chloropropionic acid. Treatment of the product acid with aqueous ethanolic solium bicarbonate gives triphenylphosphonopropionbetaine in high yield [13]:

$$[(C_6H_5)_3P(CH_2)_2CO_2H]^+Cl^- + NaHCO_3 \rightarrow$$
$$(C_6H_5)_3P^+(CH_2)_2CO_2^- + CO_2 + H_2O + NaCl \quad (3)$$

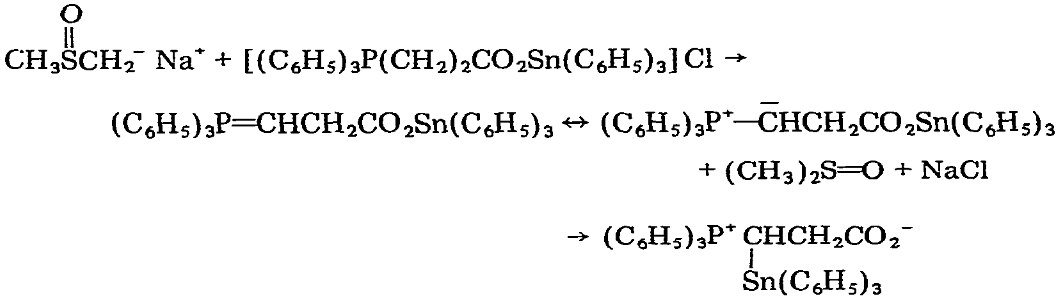
Table 1 lists the various triphenylphosphonopropionbetainetriorganotin(IV) salts that were prepared by the novel nucleophilic displacement together with their analytical data and percentage yield. Most of the triphenyltin derivatives are high melting solids (with decomposition), and the similarity of the temperatures suggests that it is the common triphenylphosphonopropionbetainetriphenyltin cation that undergoes decomposition in each case. All the compounds are white except for the tetracarbonylcobaltate and diphenyl(8-hydroxyquinolinato)tin derivatives which are brown and yellow-colored solids, respectively.

Since the triphenylphosphonopropionbetainetriorganotin complexes can be prepared in good yield by reaction pathway 2, we thought it worthwhile to attempt further reactions on the triphenyltin(IV) chloride derivative.

The attempt to dehydrochlorinate the phosphonium salt, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+Cl^-$, by treatment with methylsulfinyl sodium from sodium hydride in dimethylsulfoxide [28] gave instead the double salt, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+[(C_6H_5)_3SnCl_2]^-$ as the only tin containing product. We had anticipated the formation of the ylid which would displace the triphenyltin group from the carboxylate to form a carbon—tin bond through the phosphorus ylid as has been previously reported [33]:



$$\mathrm{NaH + (CH_3)_2S{=}O \rightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{S}CH_2^- \, Na^+} \qquad (4)$$



$$\mathrm{CH_3\overset{\overset{\displaystyle O}{\|}}{S}CH_2^- \, Na^+ + [(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]Cl \rightarrow}$$
$$\mathrm{(C_6H_5)_3P{=}CHCH_2CO_2Sn(C_6H_5)_3 \leftrightarrow (C_6H_5)_3P^+{-}\bar{C}HCH_2CO_2Sn(C_6H_5)_3}$$
$$\mathrm{+ (CH_3)_2S{=}O + NaCl} \qquad (5)$$
$$\mathrm{\rightarrow (C_6H_5)_3P^+ \underset{\underset{\displaystyle Sn(C_6H_5)_3}{|}}{C}HCH_2CO_2^-}$$

Such a compound would function as a precursor in the preparation of compounds with three tin atoms in the molecule, all in different environments. The attempt to prepare the methyltin(IV), double salt, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(CH_3)_3]^+ [(CH_3)_3SnCl_2]^-$, by concentrating a solution of the ylid and organotin(IV) chloride in a 1/2 ratio gave only an oil which could not be crystallized.

The acetate derivative could be prepared through a simple metathesis reaction from lead(II) acetate:

$$\mathrm{2[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+Cl^- + Pb(CH_3CO_2)_2 \rightarrow}$$
$$\mathrm{2[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ \, CH_3CO_2^- + PbCl_2} \qquad (6)$$

Triphenylphosphonopropionbetainetriphenyltin(IV) chloride loses carbon dioxide at its melting point of 191°C, presumably to produce the corresponding 2-(triphenylstannyl)ethyltriphenylphosphonium chloride:

$$\mathrm{[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+Cl^- \rightarrow}$$
$$\mathrm{CO_2 + [(C_6H_5)_3P(CH_2)_2Sn(C_6H_5)_3]^+Cl^-} \qquad (7)$$

Proton NMR data

Most of the carboxylates prepared in this study are too insoluble in common NMR solvents to give meaningful results, with the exception of the species listed in Table 3. In deuterated chloroform, the methyl signal of $[(C_6H_5)_3P(CH_2)_2CO_2Sn(CH_3)_3]^+Cl^-$ appears at δ 0.64 ppm, relative to TMS and the $|^2J(^{119}\mathrm{Sn{-}C{-}}^1\mathrm{H})|$ coupling constant is 72.8 Hz. We are unable to prepare the double tin salt $[(C_6H_5)_3P(CH_2)_2CO_2Sn(CH_3)_3]^+ [(CH_3)_3SnCl_2]^-$, but a deuterochloroform solution of $[(C_6H_5)_3P(CH_2)_2CO_2Sn(CH_3)_3]^+Cl^-$ and $(CH_3)_3SnCl$ in a 1/2 stoichiometry displays only one methyl signal at δ 0.64 ppm, and $|^2J(^{119}\mathrm{Sn{-}C{-}}^1\mathrm{H})|$ is decreased to 64.5 Hz.

The compound $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_2CH_3]^+ [CH_3(C_6H_5)_2SnCl_2]^-$ shows a $|^2J(^{119}\mathrm{Sn{-}C{-}}^1\mathrm{H})|$ coupling constant of 76.0 Hz compared with 60.0 Hz for $(CH_3)(C_6H_5)_2SnCl$. As with the trimethyltin case, only one methyl signal is observed at δ 1.00 ppm.

Mössbauer data

Table 2 lists the Mössbauer parameters of the compounds prepared. The IS and QS values are consistent with five-coordinated triorganotin formulations [32], with the exception of triphenylphosphonopropionbetainediphenyl(8-hydroxyquinolinato)tin(IV) chloride, which is probably six-coordinated. Since the QS for the latter is ca. 2 mm s^{-1}, the two phenyl groups must be *cis* to each other. Diaryltin compounds can adopt either a *cis*- or a *trans*-configuration in their complexes, whereas with the dialkyl analogues, the carbon—tin—carbon skeleton is almost invariable linear [7]. The carbon—tin—carbon angle in our diphenyltin(IV) chloride can be calculated from a point charge approach [34] that assumes that the partial QS contributions from the ligands will be small compared to that from the phenyl groups, and the correlation is supported by data from compounds for which both Mössbauer and diphenyltin(IV) carbon—tin—carbon angles are available [35]. On this basis we predict an angle of 109° for the diphenyltin system in our derivative.

In the series $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+X^-$ where the X group is varied from the potentially bridging halide, pseudohalide, acetate, nitrate, etc., to the essentially non-nucleophilic tetraphenylborate anion, there appears to be not much variation in the Mössbauer parameters. Thus the X groups are probably not bonded directly to the tin atom, but exist as counterions. Hence, the compounds should be formulated as phosphonium salts in which one of the organic groups on the phosphorus atom is an organotin-containing carboxylate residue.

In the series of compounds with tin both in the cation and anion, the Mössbauer spectra are best fitted by only one symmetrical doublet, and the IS and QS values are close to the values obtained for the previous tin cation series. It seems, therefore, that either the electronic environments about the tin nuclei are identical, or that the whatever differences there are cannot be detected by tin-119m Mössbauer spectroscopy.

It is interesting to note in this connection that the compound $[(CH_3)_2SnCl_2]_2$ terpyridyl exists as a double salt $[(CH_3)_2SnCl \cdot \text{terpyridyl}]^+ [(CH_3)_2SnCl_3]^-$ with the tin cation in an octahedral environment and the tin anion in a trigonal bipyramidal environment [36] but exhibits only one doublet in its Mössbauer spectrum [37].

Infrared data

Table 5 contains the infrared absorptions for the compounds obtained, and the absorptions which can be assigned to the carboxylate system are listed in Table 4.

The tin—carbon and tin—oxygen modes below 600 cm^{-1} cannot be unambiguously assigned because the phosphonobetaine moiety itself has a rich spectrum in this region. Triphenylphosphonopropionbetaine absorbs at 1593 and 1583 cm^{-1}, and in the complexes the asymmetric CO_2 stretch is observed near 1645 cm^{-1} for the $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+X^-$ compounds and 1585 cm^{-1} for the $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3SnX_2]^-$ compounds. The lowered values in the latter series would suggest that stronger association by the carboxylate oxygens is taking place there. The slightly lesser degree of association in the first series can be interpreted in terms of some steric hindrance arising from the proximity of the counterion to the tin atom rather than to the

TABLE 2

TIN-119m MÖSSBAUER DATA FOR THE TRIPHENYLPHOSPHONOPROPIONBETAINETRIORGANOTIN(IV) SALTS (at 77 K in mm s^{-1})

Compound	IS ± 0.03	QS ± 0.06	Γ ± 0.03	ρ = QS/IS
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(CH_3)_3]^+ Cl^-$	1.30	3.45	1.35	2.65
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ Cl^-$	1.22	2.90	1.24	2.38
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ Br^-$	1.26	3.00	1.05	2.38
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ I^-$	1.10	2.98	1.45	2.95
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ NCS^-$	0.96	3.05	1.28	3.18
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ N_3^-$	1.00	3.01	1.22	3.01
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ NO_3^-$	1.25	3.23	0.89	2.58
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ CH_3CO_2^-$	1.19	2.90	1.32	2.44
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ B(C_6H_5)_4^-$	0.98	3.06	1.60	3.12
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ Co(CO)_4^-$	1.21	2.96	1.17	2.45
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_2(C_9H_6NO)]^+ Cl^-$	0.71	2.17	2.15, 3.18	3.06
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3SnCl_2]^-$	1.05	3.14	1.41	2.99
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3SnBr_2]^-$	1.09	3.16	1.21	2.90
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3Sn(N_3)_2]^-$	1.02	3.10	1.50	3.04
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3Sn(NCO)_2]^-$	0.98	2.92	1.14	2.98
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(CH_2Sn)(C_6H_5)_2]^+ [(CH_3)(C_6H_5)_2SnCl_2]^-$	1.35	3.36	2.55	2.49
$[(C_6H_5)_3PS(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3SnCl_2]^-$	1.28	3.15	1.02	2.45

TABLE 3

NMR DATA FOR THE METHYLTIN(IV)-CONTAINING DERIVATIVES

	$\delta(CH_3)$ (ppm)	$\lvert {}^2J({}^{119}Sn\text{—}C\text{—}{}^1H)\rvert$(Hz)
$(CH_3)_3SnCl(CDCl_3)$	0.69 [a]	57.8 [b]
$[(CH_3)_3SnO_2C(CH_2)_2P(C_6H_5)_3]^+ Cl^-$	0.64	72.8
plus 1/1 $(CH_3)_3SnCl$	0.64	64.5
$CH_3(C_6H_5)_2SnCl$	0.88	60.0
$[CH_3(C_6H_5)_2SnO_2C(CH_2)_2P(C_6H_5)_3]^+$ $[CH_3(C_6H_5)_2SnCl_2]^-$	1.00	76.0

[a] Ref. 50. [b] Ref. 51.

phosphorus atom. Tin is a hard acid, and although organic groups confer some degree of softness, it retains its hard character, and it is, therefore, not surprising that the counterion would be found to be within possible interaction distance of the tin atom rather than the phosphorus atom.

The compound $[(C_6H_5)_3P(CH_2)_2CO_2Sn(CH_3)_3]^+ Cl^-$ exhibits an asymmetric CO_2 band at 1616 cm^{-1}. The effect of lowered mass is unlikely to predominate in this case, and it appears that because of decreased steric crowding about the

TABLE 4

INFRARED ABSORPTIONS FOR THE CARBOXYLATE SYSTEM IN TRIPHENYLPHOSPHONOPROPIONBETAINETRIORGANOTIN SALTS (cm^{-1})

	$\nu_{asym}(CO_2)$	Other ν's
$(C_6H_5)_3P(CH_2)_2CO_2$	1593, 1583	
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(CH_3)_3]^+ Cl^-$	1616	
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ Cl^-$	1643	
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ Br^-$	1647	
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ I^-$	1646	
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ NCS^-$	1646	2050 (ν(NCS)) [a]
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ N_3^-$	1642, 1586, 1548	2075, 2065, 2045 ($\nu(N_3)$ [b]
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ NC_3^-$	1648	$\nu(NO_3)$ cannot be located
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ CH_3CO_2^-$	1645	
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ B(C_6H_5)_4^-$	1646	
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ Co(CO)_4^-$	1635, 1585	1885 (ν(CO)) [c]
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_2(C_9H_6NO)]^+ Cl^-$	1585, 1575, 1560	
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+$ $[(C_6H_5)_3SnCl_2]^-$	1600, 1585, 1575	
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+$ $[(C_6H_5)_3SnBr_2]^-$	1587, 1575, 1557	
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+$ $[(C_6H_5)_3Sn(NCO_2]^-$	1587, 1574, 1569	2075, 2065 ($\nu(N_3)$ [b]
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+$ $[(C_6H_5)_3Sn(NCO_2]^-$	1645	2206 (ν(NCO)) [d]
$[(c_6H_5)_3P(CH_2)_2CO_2Sn(CH_3)(C_6H_5)_2]^+$ $[(CH_3)(C_6H_5)_3SnCl_2]^-$	1585, 1575, 1560	
$[(C_6H_5)_3PS(CH_2)_2CO_2Sn(C_6H_5)_3]^+$ $[(C_6H_5)_3SnCl_2)^-$	1585, 1575, 1560	

[a] The ν(NCS) mode in $(C_6H_5)_3$ SnNCS is at 2080 cm^{-1}. [b] The $\nu(N_3)$ mode in $(C_6H_5)_3SnN_3$ is at 2100, 2080, 2065 cm^{-1}. [c] The ν(CO) mode in $(C_6H_5)_3SnCo(CO)_4$ is at 1890 cm^{-1}. [d] The ν(NCO) mode in $(C_6H_5)_3SnNCO$ is at 2230 cm^{-1}.

TABLE 5

INFRARED ABSORPTIONS (cm^{-1})[a,b]

$[(C_6H_5)_3P(CH_2)_2CO_2H]^+ Cl^-$	1436s, 1418m, 1406m, 1357s,br, 1278m, 1218s, 1190m, 1161m, 1112s, 1032m, 994m, 947m, 908m, 856m, 812m, 750s, 737s, 727s, 681s, 533m, 504m, 474s, 428m
$(C_6H_5)_3P(CH_2)_2CO_2$	1468vs, 1439vs, 1305w, 1112s, 996m, 958w, 911m, 806w, 706s, 750s, 697s, 688s, 514m, 503m, 489m
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(CH_3)_3]^+ Cl^-$	1587m, 1437vs, 1342m, 1299m, 1283s, 1215m, 1194w, 1180m, 1159m, 1105vs, 996s, 767sh, 746vs, 728vs, 688s, 586w, 490s,br, 438w
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ Cl^-$	1436s, 1375s, 1287s, 1192m, 1110s, 1167m, 996m, 797w, 749vs, 698s, 510m, 495m, 442m
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ Br^-$	1400s, 1358s, 1290m, 111m, 740s, 698m, 510m,br, 445m,br
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ I^-$	1441s, 1357m, 1289m, 1111m, 739m, 698m, 687m, 511m,br, 498m, 442m
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ NCS^-$	1439s, 1355s, 1113s, 740s, 697s, 689sh, 512w,br
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ N_3^-$	1439s, 1355w, 1068vs, 730s, 695s, 498m,br, 445m,br
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ NO_3^-$	1440vs, 1357s, 1300s, 1290s, 1275m, 1260m, 1113s, 1025m, 996m, 737s, 700m, 687m, 515m, 445m
$[(C_6H_5)_3P(CH_2)CO_2Sn(C_6H_5)_3]^+ CH_3CO_2^-$	1440s, 1365s, 1355sh, 1315m, 1387m, 1108s, 735s, 696s, 686sh, 508m, 490sh
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ B(C_6H_5)_4^-$	1439s, 1355s, 1287m, 1111m, 732m, 699m, 685sh, 605w,br, 510w,br
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ Co(CO)_4^-$	1438s, 1362m, 1289m, 1111s, 995m, 735s, 685s, 545s, 510m,br
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_2(C_9H_6NO)]^+ Cl^-$	1495s, 1428s, 1326vs, 1280s, 1110vs, 1073m, 822m, 804m, 785m, 728vs, 695vs, 500m, 437m
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+$ $[(C_6H_5)_3SnCl_2]^-$	1442m, 1430m, 1315m, 748m, 729s, 695s, 496w,br, 445w,br
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+$ $[(C_6H_5)_3SnBr_2]^-$	1442m, 1309m, 1115m, 767m, 727s, 692s, 495w,br, 445w,br
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+$ $[(C_6H_5)_3Sn(N_3)_2]^-$	1440s, 1112w, 729m, 695m, 495w,br, 445w,br
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+$ $[(C_6H_5)_3Sn(NCO)_2]^-$	1428s, 1290m, 1112m, 1075m, 997m, 912m, 894m, 693vs, 500w,br, 440w,br
$[(C_6H_5)_3PS(CH_2)_2CO_2Sn(C_6H_5)_3]^+$ $[(C_6H_5)_3SnCl_2]^-$	1480vs, 1442vs, 1428vs, 1114m, 745m, 690vs, 492w,br, 440w,br
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(CH_3)(C_6H_5)_2]^+$ $[(CH_3)(C_6H_5)_2SnCl_2]^-$	1442vs, 1110s, 730vs, 690vs, 500m, 440w,br

[a] Recorded as Nujol Mulls on KBr plates and polystyrene film. [b] s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad.

tin atom, the strength of the carboxylate bridging is greater than in the triphenyltin case.

When the X group, as with the pseudohalide and $Co(CO)_4$ groups, also absorbs in the infrared, we have been able to record the shift of the bands to lower energies upon complexation. Of the various anions studied, the most informative is the tetracarbonylcobaltate because the geometry of the moiety can be deduced from the absorption bands of the carbonyl group [38]. In the ionic form the moiety has tetrahedral symmetry and a single absorption band for ν(CO) in the infrared. On the other hand, bonding the tin atom to the cobalt lowers the symmetry of that group in such compounds as $(C_6H_5)_3SnCo(CO)_4$ [7]. In a polar solvent such as acetone, however, this compound dissociates to the solvated triphenyltin cation and the tetracarbonylcobaltate anion [38], the latter exhibiting a single carbonyl stretching absorption at 1890 cm^{-1}. In our complex, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ Co(CO)_4^-$, we observe a single carbonyl absorption band at 1885 cm^{-1} in the solid state (1870 cm^{-1} in acetone). It appears, therefore, that the cobaltate moiety is tetrahedral and hence anionic and is not coordinated to tin.

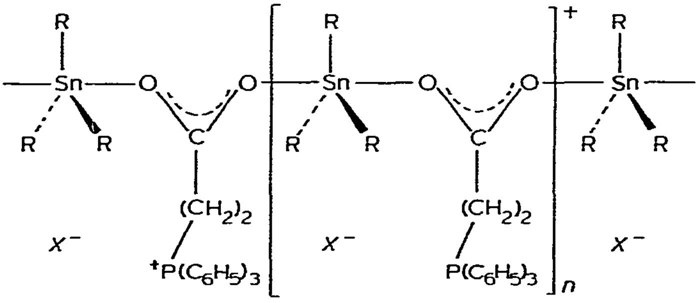
Whereas the infrared spectra of our salts below 600 cm^{-1} do not yield significant structural information because of the strong phosphonium ligand absorptions, the Raman spectra of these $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+X^-$ compounds are much more informative. The Raman spectra for the X = Cl, Br, I derivatives in the region 350 and 50 cm^{-1} are virtually identical as can be seen in Table 7 from which we infer that no substantive tin—halogen interactions are present, and that our products are true salts.

Structural conclusions

We infer from the tin-119m Mössbauer data that the tin atoms in our compounds are in a five-coordinated geometry in all but the 8-hydroxyquinoline complex which is probably six-coordinated and octahedral, and from the small magnitude of the QS value contains a *cis*-diphenyltin system [35]. That the spectra are doublet in nature for the others serves to rule out the possibility that our compounds are derivatives of the ylid structures, B, (vide supra), since these tetraorganotin(IV) species would give singlets only [32], and can instead be formulated as phosphobetaines with the tin groups bonding through the carboxylate oxygen atoms. The absence of ambient temperature Mössbauer spectra do not rule out bridging rather than chelating forms, and the question of involvement of the anion group, X, arises. Interaction with groups such as the $B(C_6H_5)_4$ is ruled out, however; yet the Mössbauer data for this derivative are not different. A more decisive test involves the tetracarbonylcobaltate derivative, where the infrared spectrum of the transition metal moiety is conclusive for tetrahedral symmetry and hence no interaction with the tin atom. The identical Raman data for the halides in the low frequency region are corroboratory in this regard. Conductivity measurements in dimethylformamide for $[(C_6H_5)_3SnO_2C(CH_2)_2P(C_6H_5)_3]^+Cl^-$ give a molar conductivity value, Λ_m 48 Ω^{-1} cm^{-1} M^{-1}, characteristic of a 1/1 electrolyte which can be compared with 65 Ω^{-1} cm^{-1} M^{-1} for the known ionic complex $SnCl_4 \cdot 2$ SalH-*N-para*-tolyl in the same solvent [39]. Thus we formulate these systems as salts.

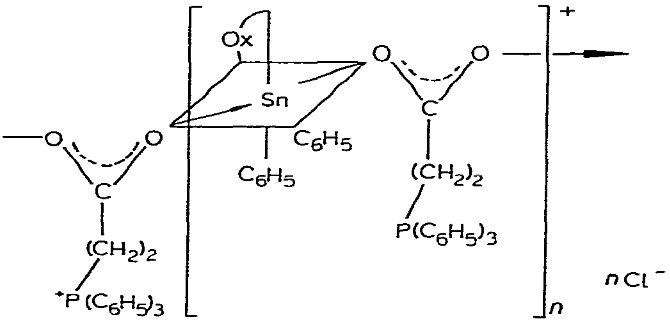
Tin bonding through the acetate group in a five-coordinated form suggests an association through oxygen atoms bridging flat trimethyltin(IV) groups in the universal, axially-most-electronegative trigonal bipyramidal configuration. Unfortunately, infrared absorption bands of the ligand obscure the $\nu(SnC_3)$ mode region, and deny us the information necessary to decide whether the trimethyltin(IV) moiety is truly planar. The lowered infrared $\nu(CO_2)$ absorption frequencies for the acetate group support the suggestion of the use of both the carboxylate oxygens in coordination to tin, most likely in the well-known bridging acetate form [7].

Our structural proposal for these systems is presented in C in which a polymeric chain of bridging carboxylate groups contains dangling triphenylphosphonium cations:



(C)

The 8-hydroxyquinolatodiphenyltin(IV) derivative, on the other hand, is, from the very low IS value, six-coordinated at tin, and the magnitude of its Mössbauer QS value specifies a *cis*-diphenyltin configuration. The quinolinato group will chelate in a *cis*-fashion, too, but this does not serve to determine the connectivity of the bridging carboxylate. We write structure D in a *cis*-, *cis*-, *trans*-configuration without wishing to specify the way in which the carboxylate groups are bound:



(D)

The double salts with triorganotin residues in both the anion and cation should behave in a straight forward manner structurally, with their solids composed of tin anions and cations, both trigonal bipyramidal. The $[R_3SnCl_2]^-$ anion has been characterized structurally for R = CH_3 in the $[Mo(h^5\text{-}C_5H_5)_3S_4]^+$ salt [40], and the structure of the trigonal bipyramidal $[(CH_3)_2SnCl_3]^-$ anion is known in its double salt with the $[(CH_3)_2SnCl \cdot \text{terpyridyl}]^+$ cation [36], but no double salts are known so far as we are aware with tin in both a trigonal bipyramidal anion and cation [7].

The spectroscopic evidence, however, presents a more puzzling picture. The

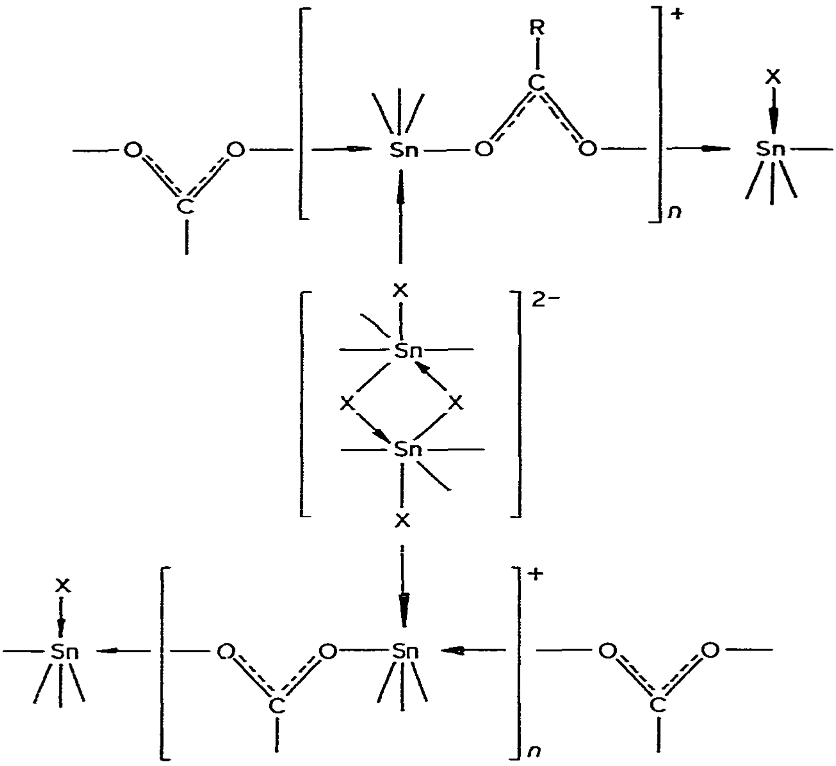
Mössbauer spectra of all the double salts contain only a simple doublet. We have seen this before for the double salt $[R_2SnCl \cdot \text{terpyridyl}]^+[R_2SnCl_2]^-$ discussed above where surprisingly well-defined doublets are recorded for the bent *trans*-dimethyltin(IV) octahedral cation and the trigonal bipyramidal anion combination where R = CH_3, n-C_4H_9 and C_6H_5 [37]. More recently we have observed the same phenomenon for the terpyridyl adducts of the dihalotetraphenylstannoles [41]. The sole similarity linking the positive and negative ions in these cases which produce superimposable spectra is the number of bonds tin makes to carbon, and the nature of the attached organic groups. In the phosphonium salts studied here the differences should be less severe since both ions are five-coordinated, presumably axially-most-electronegative with a relatively planar triphenyltin(IV) system at the equator of the ion. Yet, a direct comparison of the Mössbauer data for the phosphonium cation halide or pseudohalide salt and those for the double salts as presented in Table 6 reveal a larger linewidth and a QS value somewhat higher for the latter, both being outside experimental error. The IS values for the double chloride and bromide salts are also smaller outside experimental error. These data taken together seem to indicate that the tin atoms in these double salts may be in a higher coordinated situation than in their simple precursor salts, but we have no suggestion which we find compelling for how this could come about. Anion—cation bridging by chloride, bromide or azide groups, while certainly possible for these five-coordinated species unlike in the six-coordinated R_2Sn cations we have studied before [37,41], would have to be coupled to a similar bridging of the anion to bring the tin atoms in these species to a six-coordinated state as well. This situation seems to us unlikely since there is little precedence for triorganotin moieties being complexed by more than one donor atom to form R_3SnL_3 species, although the complexing moieties here bear opposite charges which would assist in their pairing. Indeed, in the solid quinolinium trichlorodimethylstannate(IV), $[C_9H_8N]^+[(CH_3)_2SnCl_3]^-$, there is a close contact between tin and chlorine of neighboring anions at 3.486 Å to form dimeric dianionic units containing six-coordinated tin atoms [42]. In addition, the structure of diphenyltin(IV) dichloride [43] has been reinterpreted in terms of tetrameric units containing terminal, four-coordinated molecules, one of whose chlorine atoms forms a single bridge to the two central molecules which engage in four-center bridging between them to

TABLE 6

COMPARISON OF THE MELTING POINTS (°C), AND TIN-119m MÖSSBAUER DATA FOR THE HALIDE AND AZIDE SIMPLE AND DOUBLE SALTS (in mm s^{-1} at 77 K)

	Mp (°C)	IS ± 0.03	QS ± 0.06	Γ ± 0.03
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ Cl^-$	195—197	1.22	2.90	1.25
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3SnCl_2]^-$	188—190	1.05	3.14	1.41
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ N_3^-$	154—155	1.00	3.01	1.22
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3Sn(N_3)_2]^-$	152—153	1.02	3.10	1.50
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ Br^-$	183—184	1.26	3.00	1.05
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3SnBr_2]^-$	183—184	1.09	3.16	1.21

produce six-coordination at tin [44]. Triphenyltin(IV) chloride on the other hand, forms a crystal of monomers [45]. In our more favorable electrostatic situation, dimeric $[(C_6H_5)_3SnX_2]_2^{2-}$ units could cross-link the linear, carboxylate-bridged polymers by bridging the tin atoms in two chains to produce structure E in which all the tin atoms are now six-coordinated of the R_3SnXO_2 type:



(E)

Trimethyltin(IV) chloride [46] and azide [47,48] form singly bridged solids. The additional interactions depicted in E are not reflected in higher melting points of these double salt solids.

The NMR evidence presented in Table 7 is even more puzzling. Unfortunately, we could not isolate either the double salt based upon trimethyltin(IV) chloride or the simple salt derived from methyldiphenyltin(IV) chloride, but both mixtures of the simple salt of the former and additional trimethyltin chloride in a 1/2 ratio, or the latter double salt give single sets of sharp NMR resonances with tin-117 and -119 satellites. The chemical shifts stay relatively

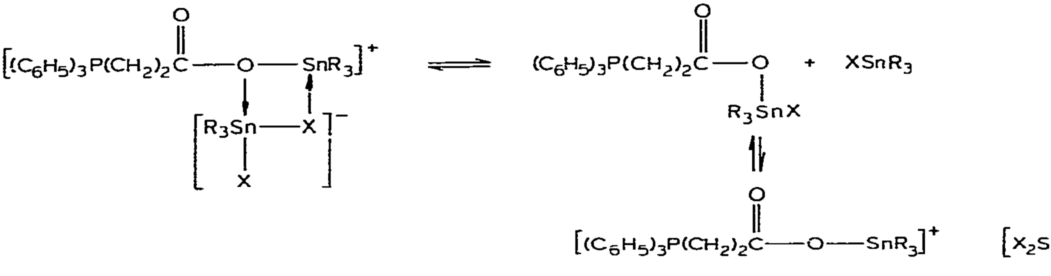
TABLE 7

RAMAN DATA FOR THE SIMPLE HALIDE SALTS BETWEEN 350 AND 50 cm^{-1}

$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ Cl^-$	255, 205, 70
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ Br^-$	255, 202, 70
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ I^-$	255, 202, 70

constant in going from the simple chloride to the phosphonium chloride salt to the double salt, but the coupling constants, which are potentially more informative about the structural situation at the tin atom, tell a confused story since in the trimethyltin case the phosphonium chloride salt value is indicative of coordination higher than four at tin, but this value drops on adding trimethyltin chloride. However, the double salt of the methyldiphenyltin derivative exhibits a coupling constant consistent with higher coordination.

The simple NMR signals observed for each of these double salts must result from either the identity of the *s*-electron density directed along the methyl—tin axes in the equatorial positions of the trigonal bipyramidal anion and cation or from a dynamic process which could scramble the two tin sites. The former is unlikely given the sensitivity of the NMR technique to small changes, but structures such as E could serve as intermediates in a process by which chlorine and oxygen attachments are exchanged via four-centered interactions as in the equilibria involving ion pairing in F, followed by dissociation and chloride exchange steps:



(8)

(F)

The R_3Sn group remains intact throughout the processes described in eq. 8 and thus the NMR $|^2J(^{119}Sn—C—^1H)|$ couplings are observed in the methyltin case.

To probe the possibility of such interactions, we recorded the variation of the tin—methyl coupling constant of trimethyltin chloride in a chloroform solution of trimethyltin chloride and triphenylphosphonopropionbetaine and the data are listed in Table 8. It is seen that the coupling constant decreases when

TABLE 8

VARIATION OF THE NMR TIN—METHYL COUPLING CONSTANT IN TRIMETHYLTIN(IV) CHLORIDE IN CHLOROFORM SOLUTIONS OF $(C_6H_5)_3P(CH_2)_2CO$

$\frac{[(CH_3)_3SnCl]}{[(CH_3)_3SnCl] + [(C_6H_5)_3P(CH_2)_2CO_2]}$	$\|^2J(^{119}Sn—C—^1H)\|$ (Hz)
0.299	71.8
0.442	71.8
0.483	70.4
0.646	67.8
0.680	66.6
0.710	64.8
0.783	64.4
0.814	63.8
0.834	63.8

the proportion of the organotin chloride is in excess of the 1/1 stoichiometry. Only one methyl signal is observed. The widths at half-height of these resonances are ca. 1 Hz.

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