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SECURITY CLASSIFICATION OF THIS PAGE (When Date READ INSTRUCTIONS REPORT DOCUMENTATION BEFORE COMPLETING FORM 1. REPORT NUMBER RECIPIENT'S 11 4. TITLE (and Subtitle) S. TYPE TEPORT ERIOD COVERED Phosphoric Acid Derivatives of Tin. I. Triorgano-MA075453 tin(IV) Dithiophosphate Esters. 6. PERFORMING ORG. REPORT NUMBER A07458 nv 8. CONTRACT OR GRANT NUMBER(+) 7. AUTHOR(.) J. L. Lefferts, K. C. Molloy and J. J. Zuckerman I. Haiduc, C. Guta and D. Ruse N00014-77-C-0432 . PERFORMING ORGANIZATION NAME AND ADDRESS 10. PROGRAM ELEMENT. PROJECT. AREA & WORK UNIT NUMBERS University of Oklahoma 1039122 Department of Chemistry NR 053-636 Norman, Oklahoma 73019 12. REPORT DATE 1. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 17 September, 1979 Department of Navy 13. NUMBER OF PAGES 25 Arlington, Virginia 22217 15. SECURITY CLASS. (of this report) 14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office) Unclassified 15. DECLASSIFICATION DOWNGRADING 16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release, Distribution Unlimited 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Prepared for Publication in Inorganic Chemistry DOC FILE COPY OCT 25 1979 18. SUPPLEMENTARY NOTES 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Organotins, Phosphoric Acids, Dithiophosphoric Acids, Esters, Synthesis, Condensation Reactions, Protodemetalation, Infrared Spectroscopy, Raman Spectroscopy, Mössbauer Spectroscopy, Tin-119m Mössbauer, Lattice Dynamics, Effective Vibrating Mass Model, Monodentate Ligands, Monodentate Dithiophosphate Ester Ligands, Nuclear Magnetic Resonance. 0. ABSTRACT (Continue on reverse side II necessary and identify by block number) Twelve triorganotin dithiophosphate esters,  $R_3SnS_2P(OR')_2^2$ , where  $R=C_6H_5$ - and  $R'=CH_3$ -,  $C_2H_5$ -,  $n-C_3H_7$ -,  $i-C_3H_7$ -,  $n-C_4H_9$ -,  $i-C_4H_9$  and  $C_6H_5$ -; and  $R=CH_3$ - and  $R'=CH_3$ -,  $C_2H_5^2$ ,  $n-C_3H_7^2$  and  $i-C_3H_7$ -; and  $R-C_6H_{11}$ - and  $R'=i-C_3H_7$ - were synthesized in high yield by the condensation of the organotin hydroxide with the 0, diorganodithiophosphoric acid to release water which was distilled azeotropically, or taken up in an alcohol solvent corresponding to the phosphoric acid ester group, or by the reaction of the triorganotin chlorides with an alkali metal salt of the dithiophosphoric acid. The products are colorless DD 1 JAN 73 1473 EDITION OF I NOV 65 IS OBSOLETE Unclassified S/N 0102-LF-014-6601 SECURITY CLASSIFICATION OF THIS PAGE (Phon Data Entere.

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Phosphoric Acid Derivatives of Tin. I. Triorganotin(IV) Dithiophosphate Esters.

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#### ABSTRACT

Twelve triorganotin dithiophosphate esters,  $R_3SnS_2P(OR')_2$ , where  $R=C_6H_5$ - and R'=CH3-, C2H5-, n-C3H7-, 1-C3H7, n-C4H9-, 1-C4H9 and C6H5-; and R=CH3- and R'=CH3-,  $C_2H_5$ , n- $C_3H_7$ - and i- $C_3H_7$ -; and R= $C_6H_{11}$ - and R'=i- $C_3H_7$ - were synthesized in high yield by the condensation of the organotin hydroxide with the 0,0'-diorganodithiophosphoric acid to release water which was distilled azeotropically, or taken up in an alcohol solvent corresponding to the phosphoric acid ester group, or by the reaction of the triorganotin chlorides with an alkali metal salt of the dithiophosphoric acid. The products are colorless, crystalline solids except for the trimethyltin derivatives which are oils. The synthesis of the diisopropyl ester in the triphenyltin series was accompanied by protodemetalation to yield the bis-compound,  $(C_6H_5)_2Sn[S_2P(0C_3H_7-i_2)]_2$ . Infrared spectral bands were assigned to the vCO(1170-1095),  $v_{asym} PS_2(675-635)$ , and vPOR (1015-965) cm<sup>-1</sup>, but the  $v_{sym}$  PS<sub>2</sub> absorption obscures the  $v_{sym}$  SnC<sub>3</sub> modes. Nmr  $|^2 J(^{119}Sn-C-^{1}H)|$  coupling constants for the methyltin series are consistent with four-coordinated tin in solution, and mass spectral data with monomers. Tin-119m Mössbauer data, on the other hand, specify a five-coordinated structure for the methyltins, but four-coordinated for the cyclohexyl-and phenyltins. The triphenyltin ethoxy and isopropoxy derivatives behave identically in a variable-temperature Mössbauer study, where the slope of the temperature-dependence of the log of the resonance area is consistent with a monomeric structure packed in the solid into a rather tight lattice. Using low-energy, lattice-mode Raman data in the effective vibrating mass treatment, the molecularity of the vibrating unit is found to be monomeric. The predicted monomeric, monodentate structure for these two esters is unique among dithiophosphate-metal systems.

Organotin compounds are powerful biocides, and have found wide application as agricultural fungicides and miticides, surface disinfectants, anthelminthics and marine antifouling agents.<sup>1,2</sup> A particularly intriguing idea is to combine the triorganotin moieties which show the strongest biocidal activity with organophosphorus moieties which are also known for their potent biocidal effect. The combination of the two kinds of biological activity in a single molecule could produce a still more powerful and lasting effect, and prevent the problems associated with the development of tolerance to each kind.

Several model organotin dithiophosphorus systems suggest themselves as subjects for study. We initiate this series of papers with a description of the synthesis of the triorganotin dithiophosphate esters. This class of compounds was first introduced in 1964<sup>3</sup>, and has been the subject of several patents describing applications as bactericides, insecticides, fungicides, etc.,<sup>4-15</sup> but a satisfactory answer to the question of the structure-function relationships in the known systems<sup>16-19</sup> has not yet been given. The systems are also of interest structurally<sup>20</sup> since several modes of attachment of the dithiophosphate ester ligand are in principle possible, including as a monodentate, bidentate, bridging in an oligomeric form as in a dimer or as a bridging ligand in an associated polymer chain. The X-ray crystallographic results for certain key examples will be published as a part of this series.

We report here the synthesis of 12 compounds, nine not reported before, by two preparative methods.

#### Experimental Section

Reagent grade chemicals and solvents were used as received, except for triphenyltin chloride (M&T) which was recrystallized from chloroform before use. Trimethyltin hydroxide was prepared from the chloride. Infrared spectra were recorded as KBr discs or Nujol mulls on KBr plates and polyethylene film on Beckman 4250 or IR-12 spectrometers Tin-119m Mössbauer spectra were recorded at 77K on a Ranger Engineering constant acceleration spectrometer equipped with scintillation counting and with Ca<sup>119m</sup>SnO<sub>3</sub> (New England Nuclear Corp.) used both as source and zero isomer shift (I.S.) reference standard. Mass spectra were recorded on a Hewlett Packard 5985 GC/MS System at 70 ev. Raman spectra were recorded on a Spex Ramalog 5 system. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc.

The compounds studied are listed with the preparatory method used, their yields, melting points, and microanalytical data in Table I. Tin-119m Mössbauer data are listed in Table II.

## Preparation of the 0,0'-Dialkylphosphorodithioic Acids, HS(S)P(OR').

Tetraphosphorus decasulfide (444.5g, 1 mole) was treated with the corresponding anhydrous alcohol (4 moles), added dropwise with magnetic stirring. Hydrogen sulfide was evolved, and the solid dissolved completely with formation of the crude acid. The reaction was exothermic and external cooling was applied at initial stages. Toward the end of the reaction, gentle warming with a water bath (<u>ca</u>. 60-80°C) was necessary to speed up the reaction. The crude acid was distilled <u>in vacuo</u> (as fast as possible to avoid decomposition) at the following temperatures:  $R=CH_3^{21,22}$ , b. 62-4°/0.5;  $C_2H_5^{21,22}$ , b. 75-8°/0.3;  $n-C_3H_7^{21,22}$ , b. 112°/0.5;  $i-C_3H_7^{21-23}$ , b. 72-4°/0.7;  $n-C_4H_9^{22,23}$ , b. 120°/0.8-1;  $i-C_4H_9^{24}$ , b. 75°-84°C/0.08-0.1torr;  $C_6H_5^{25}$ , m.p. 60-61°C.

# Preparation of the Sodium Salts, NaS(S)P(OR'), 26

Sodium 0,0'-dialkyldithiophosphates were prepared via sodium ethoxide, formed by dissolving the stoichiometric amount of metallic sodium in absolute ethanol (excess) and treating the solution with an equivalent amount of dialkyldithiophosphoric acid. The solutions were used immediately without isolation of the salt.

## Preparation of Ammonium Dialkyldithiophosphates, NH S. P(OR'), 27

Phosphorous decasulfide (88.9g, 0.2 moles) was treated with anhydrous alcohol (0.8 moles) added dropwise. After all the phosphorus decasulfide had dissolved the mixture was heated gently on a water bath until the reaction was completed. The acid thus obtained was diluted with 3-400 ml of dry benzene and a stream of anhydrous ammonia bubbled through the solution. The ammonium dialkyldithiophosphate precipitated was filtered, washed with benzene and dried. The yields were as follows:  $R'=CH_3$ , 46%;  $C_2H_5$ , 61%;  $n-C_3H_7$ , 61%;  $i-C_3H_7$ ; 70%;  $n-C_4H_9$ , 58%. Preparation of Triphenyltin Dithiophosphate Esters.

0,0 -Dimethyldithiophosphatotriphenyltin, (C6H5) 3 SnS2P(0CH3)2.

Triphenyltin chloride (7.70g, 0.02 mole) was treated with  $NaS_2^P(OCH_3)_2$  (3.6g, 0.02 mole) in methanol. The mixture was heated on a water bath for 1h, filtered and concentrated to give 3.6g (35.6%) of the product, m.p. 83° (lit. 86°C<sup>3</sup>).

Alternatively, a suspension of triphenyltin hydroxide (1.22g, 0.0033 mole) in methanol was heated with dimethyldithiophosphoric acid (0.61g, 0.004 mole) on a water bath until a clear solution was obtained, which on cooling deposited 1.2g (71.7%) of the crystalline product. m.p. 83° (lit.  $86°C^3$ ).

0,0'-Diethyldithiophosphatotriphenyltin, (C6H5) 3 SnS2P(0C2H5)2.

Triphenyltin chloride (7.7g, 0.02 mole) was similarly treated with sodium diethyldithiophosphate (4.16g, 0.02 mole) to give 6.4g of the product (60% yield), mp 105° (lit. 105°C.<sup>3</sup>).

Alternatively, a s pension of triphenyltin hydroxide (18.3g, 0.05 mole) in absolute ethanol was treated with diethyldithiophosphoric acid (9.3g, 0.05 mole) diluted with absolute ethanol and allowed to reflux for 2h. on a water bath until a clear solution was obtained. The solution was concentrated and cooled to give 21.5g (88.5% yiel product. m.p. 105° (lit. 105°C<sup>3</sup>).

# 0,0'-Di-n-propyldithiophosphatotriphenyltin, (C6H5) 3SnS2P(OC3H7-n)2

Triphenyltin chloride (3.88g, 0.02 mole) was treated in the same way with sodium di-n-propyldithiophosphate (2.36g, 0.02 mole) to yield 1.3 g of the

product (23%), mp 63° (lit. 63C.<sup>3</sup>).

Alternatively, a suspension of triphenyltin hydroxide (5.0g, 0.014 mole) in n-propanol was heated with di-n-propyldithiophosphoric acid (2.9g, 0.014 mole) until a clear solution was formed. After concentration and cooling 5.1g (65.1% yield) of produc m.p. 63° (lit. 63°C<sup>3</sup>) was obtained.

### 0,0'-Diisopropyldithiophosphatotriphenyltin, (C6H5)3SnS2P(0C3H7-i)2

A solution of the sodium salt of diisopropyldithiophosphoric acid (0.01m) in absolute ethanol (20 mL) was added dropwise to a stirred solution of triphenyltin chlorde (0.01m) in freshly distilled diethylether (70 mL). After 24 h. the white ppt. was separated by filtration through diatomaceous earth, and the filtrate concentrated to dryness on a rotary evaporator. The resulting white solid was dissolved in a minimum of warm toluene, filtered, and allowed to crystallize at 0°C, yielding white, prismatic crystals (2.93 gms. 52% yield) of the title compound. m.p. 73.5-74.5°C.

A second crop of needle-like crystals separated after several days, identified as bis-(0,0'-diisopropyldithiophosphato)diphenyltin (m.p. 110°C.) <u>Anal</u>.: Found: C,41.78; H,5.37%,  $C_{24}H_{38}O_4P_2S_4Sn$  requires: C,41.20; H,5.49%. <u>0,0'-Di-n-butyldithiophosphatotriphenyltih</u>, ( $C_6H_2$ )\_SnS\_P(OC\_4H\_9-n)\_2

A suspension of triphenyltin hydroxide (4.0g, 0.011 mole) in n-butanol was allowed to reflux for 3h. with di-n-butyldithiophosphoric acid (2.6g, 0.011 mole). The solution was concentrated and cooled, to give 6.1g (94.3% yield) of the product, m.p.  $68-9^{\circ}C$  (lit.  $69.05^{\circ}C^{3}$ ).

### 0,0'-Diisobutyldithiophosphatotriphenyltin, (C6H5)3SnS2P(0C4H9-i)2

Equimolar quantities (0.02m) of triphenyltin hydroxide and diisobutyldithiophosphoric acid were allowed to reflux together in benzene (100 mL) and the water formed azeotropically distilled into a Dean and Stark trap. Concentration of the resulting solution yielded a colorless oil, from which crystallization was induced by the addition of n-hexane at 0°C. The product was purified by recrystallization from a hexane/benzene (10:1) mixture (8.74 gms, 63%) m.p. 52-4°C.

### 0,0'-Diphenyldithiophosphatotriphenyltin, (C,H,) SnS\_P(OC,H,)

Triphenyltin hydroxide and diphenyldithiophosphoric acid in 0.02 molar quantities were allowed to reflux together in benzene (100 mL) and the water formed azeotropically distilled into a Dean and Stark separator. After 2 h. the requisite amount of water had been collected and the resulting solution was allowed to cool, filtered and concentrated to <u>ca</u>. 10mL on a rotary evaporator. The white precipitate that formed was taken up in a minimum amount of warm toluene and allowed to crystallize 0°C., yielding a white crystalline product (9.8 gms, 77% yield), identified as 0,0'diphenyldithiophosphatotriphenyltin, m.p. 121-2°C.

#### 0,0'-Dimethyldithiophosphatotrimethyltin, (CH<sub>2</sub>)<sub>3</sub>SnS<sub>2</sub>P(OCH<sub>3</sub>)<sub>2</sub>

Metallic sodium (1.20g, 0.052 mol) was dissolved in 30mL absolute ethanol and dimethyldithiophosphoric acid (8.24g, 0.052 mol) added. Trimethyltin chloride (9.50g, 0.048 mol) in absolute ethanol was added with stirring, sodium chloride filtered, and the filtrate concentrated to give the crude product as an oil. This was distilled (b.p. 75-80° C/0.01mm) to give pure product (6.35g, 42%). 0,0'-Diethyldithiophosphatotrimethyltin, (CH<sub>3</sub>)<sub>3</sub>SnS<sub>2</sub>P(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>

Method A.

Trimethyltin hydroxide (3.77g, 20.9 mmol) and diethyldithiophosphoric acid (3.94g, 21.2 mmol) were mixed in benzene (65 ml), and the solution heated at reflux for 3 h. Water produced in the reaction was collected by a Dean and Stark trap. After removal of benzene under vacuum, the product was vacuum distilled to give 4.64g (13.3 mmol, 64% yield) of the product, b.p. 112-115°C/0.2mm. Method B.

Potassium hydroxide (0.28g, 5 mmol) was dissolved in ethanol and trimethyltin chloride (0.995g, 5 mmol) added to give a precipitate. Diethyldithiophosphoric acid (0.93g, 5 mmol) was added, and the mixture refluxed for 1h. The solution was filtered and the filtrate evaporated to give 1.3g (80% yield) of the product as an oil.

# 0,0'-Di-n-propyldithiophosphatotrimethyltin, (CH3)3SnS2P(0C3H7-n)2

Potassium hydroxide (0.28g, 5 mmol) in ethanol was treated with trimethyltin chloride (0.995g, 5 mmol). After the addition of di-n-propyldithiophosphoric acid (1.02g, 4.8 mmol) the mixture was refluxed for 1 h., then filtered and the solvent evaporated to give an oil (1.37g, 75% yield).

# 0,0'-Diisopropyldithiophosphatotrimethyltin, (CH3)3SnS2P(OC3H7-iso)2

To a solution of trimethyltin chloride (3.98g, 20 mmol) in diethyl ether (30 ml) was added a solution of the sodium salt of diisopropyldithiophosphoric acid (4.86g, 20.5 mmol) in anhydrous ethanol. Formation of a white precipitate began immediately. The mixture was heated at reflux for 1 h., cooled and filtered through diatomaceous earth. Solvent was removed under vacuum on the rotary evaporator. The residual oil was purified by vacuum distillation to yield 5.65g of the product (15 mmol, 75% yield), b.p. 105-109°C/0.4mm.

#### **Results and Discussion**

The synthesis of the triorganotin dithiophosphate esters proceeds in high yield from the reaction of a triorganotin hydroxide with the 0,0'-diorganodithiophosphoric acid:

$$R_{3} \text{SnOH} + HSP(OR')_{2} \xrightarrow{\text{benzene}} R_{3} \text{SnSP}(OR')_{2} + H_{2}O$$
(1)

 $R=CH_3; R'=C_2H_5$  $R=C_6H_5; R'=C_4H_9, C_6H_5$ 

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The released water is azeotropically distilled to drive the reaction. The above reaction also proceeds in a solvent of the alcohol corresponding to the phosphoric acid ester group:

$$R_{3}SnOH + HSP(OR')_{2} \xrightarrow{R'OH} R_{3}SnS_{2}P(OR')_{2} + H_{2}O$$

$$R=C_{6}H_{5};R'=CH_{3}, C_{2}H_{5}, n-C_{3}H_{7}, n-C_{4}H_{9}$$
(2)

In addition, triorganotin chlorides react with the alkali metal salts of the dithiophosphoric acid:

$$R_{3}SnC1 + MSP(OR')_{2} \longrightarrow R_{3}SnSP(OR')_{2} + MC1$$

$$R=C_{6}H_{5}; R'=CH_{3}, i-C_{3}H_{7}; M=Na$$

$$CH_{3} i-C_{3}H_{7}, CH_{3} Na$$
(3)

These derivatives have also been synthesized by the protodemetalation of tetraorganotins:<sup>16,18</sup>

cyclo-C6H11 i-C3H7

$$R_4 Sn + HSP(OR')_2 \longrightarrow R_3 SnSP(OR')_2 + RH$$
(4)

The organotin dithiophosphate esters listed in Table I are colorless, crystalline solids, soluble in polar and non-polar solvents, except for the trimethyltin derivatives which are liquids or oils in the case of the higher esters. The synthesis of 0,0'-diisopropyldithiophosphatotriphenyltin from the sodium salt of the dithiophosphoric acid was accompanied by the cleavage of the phenyl-tin bond to produce the bis-compound.

Three different covalent structures  $(\underline{A}-\underline{C})$  must be considered for the triorganotin dithiophosphate esters:



In addition, an ionic form (D) is also possible: S R<sub>3</sub>Sn<sup>+</sup> -S-P'(OR')<sub>2</sub>

The ionic form, <u>D</u>, and the polymeric form, <u>C</u>, are improbable in view of the good solubility of the species in non-polar organic solvents. The dithiophosphate group is known to act as a bidentate ligand through sulfur in many transition metal chelate complexes, but monodentate behavior as in <u>A</u> is apparently unknown.<sup>28</sup>

Infrared data cannot distinguish between the various possibilities since it is impossible to assign with confidence the P-S and P=S stretching frequencies. Thus for the free acids  $(RO)_2^{PSH}$  and their esters  $(RO)_2^{PSR}$  the P-S stretching bands appear in the same region as for the transition metal complexes  $M[S_2P(OR)_2]_n$  which contain bidentate dithiophosphate ligands.<sup>29</sup> The P-S absorptions appear in the range 560-530 and 670-630 cm<sup>-1<sup>30</sup></sup>, and can probably best be described as  $v_{sym} PS_2$ and  $v_{asym} PS_2$ , respectively. There seems to be little sensitivity on the part of these frequencies to the groups connected to sulfur.<sup>30,31</sup>

The infrared spectral assignments for our compounds are listed in Table III. It is possible to assign with confidence only the vCO,  $v_{asym} PS_2$  and vPOR bands. The  $v_{asym} PS_2$  absorption is found in the range 675-635 for our compounds with vCO at 1170-1095 and vPOR at 1015-965 cm<sup>-1</sup>.<sup>32</sup> The  $v_{sym} PS_2$  absorptions apparently obscure the  $v_{sym} SnC_3$  region, thus denying us important information on the configuration of the triorganotin skeleton. The assignment of the vPS<sub>2</sub> modes is done by analogy with those reported for the corresponding organolead,<sup>33</sup> thallium<sup>31</sup> and mercury<sup>34</sup> derivatives.

Proton nmr data are listed in Table IV. The spectra exhibit the resonances arising from the aromatic protons in the range 7.00-8.30 ppm, and for the organic ester groups attached to phosphorus through oxygen with the expected integrated areas and spin-spin coupling constants. Thus, in the spectrum of  $(C_{6H_5})_3 SnSP(OCH_3)_2$ , the methoxy group signal appears as a doublet arising from the coupling  $|^3J(^{31}P-O-C^{-1}H)| = 15.5Hz$ , and in the ethoxy derivative the methylene protons appear as a doublet of quartets arising from the coupling  $|^3J(^{31}P-O-C^{-1}H|)|$ =10Hz and the coupling  $|^3J(^{1}H-C-C^{-1}H)| = 7.0Hz$  with the terminal methyl protons. The methyltin  $|^2J(^{119}Sn-C^{-1}H)| = 57.5Hz$  couplings are in the range expected for four-coordinated, triorganotin species in the neat liquid or dilute solutions in which they were measured.<sup>35</sup> The magnitude of this coupling increases from 57.5 to 70.0 Hz for the isopropyl ester in pyridine solution, indicative of the formation, in situ, of a five-coordinated complex with the pyridine solvent, and establishing the lower J value as corresponding to the four-coordinated situation.

The mass spectra of the three trimethyltin dithiophosphate esters show certain similarities, but the cracking pattern is very different for the 0,0'-dimethyldithiophosphate compound. In all three spectra the highest mass fragment observed arises from the loss of one methyl group from tin. In none of the spectra were there any fragments of higher mass than the monomeric species should give, nor any arising from polytin species, thus ruling out any gas phase association of these molecules. All three compounds also give prominent species at m/e 165 [(CH<sub>3</sub>)<sub>3</sub>Sn<sup>+</sup>]; in fact, this is the base peak (relative abundance 100%) for the methyl and ethyl esters.

The major pathway for decomposition of the isopropyl ester appears to be by sequential loss of the alkene from the dithiophosphate group after initial loss of CH<sub>3</sub>. from tin.

This pathway is also important for the ethyl ester, but not for the methyl since the latter has no available  $\beta$ -hydrogen for abstraction. Thus, for the isopropyl ester, prominent fragments arise from m/e 321 [(CH<sub>3</sub>)<sub>2</sub>SnS<sub>2</sub>P(OH)(OC<sub>3</sub>H<sub>7</sub>)<sup>+</sup>] and m/e 279 [(CH<sub>3</sub>)<sub>2</sub>SnS<sub>2</sub>P(OH)<sup>+</sup><sub>2</sub>, base peak] owing to loss of CH<sub>3</sub>CH=CH<sub>2</sub> twice; and for the ethyl ester, fragments at m/e 307 and 279 arise from sequential loss of CH<sub>2</sub>=CH<sub>2</sub>.

On the other hand, the dimethyldithiophosphate cannot eliminate alkene, and, therefore, appears to fragment by loss of methyl radicals from tin to give m/e 277  $[SnS_2P(OCH_3)_2^+]$  and by loss of the entire dithiophosphate group to give m/e 165  $[(CH_3)_3Sn^+$ , base peak].

a large background due to impurities arising from thermal decomposition which could not be separated by gas chromatography.

Most of the high abundance fragments are even electron ions. Odd electron ions fragement to give high abundance even electron ion by loss of radicals such as  $CH_3$  or  $(RO)_2PS_2$ . Even electron species, where possible, lose neutral alkenes to give other even electron fragments (see Scheme and Table V).

The tin-119m Mössbauer data found in Table II are consistent with triorganotin(IV) , compounds in a four-coordinated form ( $\rho$  values <1.8)<sup>36</sup> for the triphenyl- and tricyclohexyltin derivatives. The trimethyltin compounds studied display larger quadrupole splitting (QS) values which indicates that the tin atom is in a higher than four-coordinated state. This suggests, along with the nmr  $|^2J(^{119}Sn-C-^1H)|$ coupling constant data, a monomeric, weakly bidentate chelate arrangement for the solid trimethyltins at 77K as in structure <u>B</u> as one possible configuration, with the triphenyl-, tricyclohexyl- and methyltin derivatives (the latter in the liquid state) adopting the <u>A</u> structure.

Two compounds have been subjected to variable-temperature Mössbauer study, and the results are depicted in Figure 1. The Mössbauer recoil-free fraction, f, is a function of the mean-square-displacement,  $\langle x^2 \rangle$  of the tin atom from its equilibrium position:

#### SCHEME

Me3Su2b(OB)2+.

-\$2P(OR)2.

-CH3.

Me2SnS2P(OR)<sup>+</sup>2

SnS2P(OCH3)2+ m/e = 277

Me<sub>3</sub>Sn<sup>+</sup> m/e = 165

-CH3.

Me2Sn+

m/e=150 -C2H6

-CH3.

MeSn<sup>+</sup> m/e = 135 R=Et, i-Pr -alkene

 $Me_2SnS_2P(OH)(OR)^+$ 

R=Me

-C2H6

-RSH

 $Me_2SnSPO_2^+ m/e=245$ 

R=Et, i-Pr -alkene

 $Me_2SnS_2^{P(OH)} + m/e = 279$ 

-C2H6 -CH3 or CH2

> sh; SnH<sup>+</sup> Me<sub>2</sub>SnS<sub>2</sub>PO<sup>+</sup> m/e = 120, 121 m/e = 261

-H20

-H<sub>2</sub>S or H<sub>2</sub>O<sub>2</sub>

 $\frac{\text{SnS}_{2}P(OH)^{+}}{m/e^{-} 249^{2}}$ 

-C2H6

Me2SnSP02 or Me2SnS2P m/e=245

where 
$$\lambda$$
 is the wavelength of the Mössbauer gamma ray. The parameter f thus  
reflects the binding strength of the lattice. For thin absorbers, the recoil-  
free fraction is linearly related in a Debye model to the area under the resonance  
A. and its temperature dependence is given by:

$$A_{T} \{ f = \exp \left[ \frac{-6E_{R}T}{k\theta_{D}^{2}} \right]$$

 $f = \exp \left[-\frac{\langle x^2 \rangle}{x^2}\right]$ 

for  $T \ge \frac{\theta}{2}$  where  $E_R$  is the Mössbauer recoil energy and  $\theta_D$  is the Debye temperature of the solid. In the high temperature limit plots of  $\ln A_T \ vs.$  T should be linear, and the results for the two compounds studied bear this out. For  $(C_6H_5)_3 \text{SnSP}(0C_2H_5)_2$ between 77 and 150K the slope of  $-1.43 \times 10^{-2} \text{ K}^{-1}$  is based upon seven points with intercept at 1.113 and a correlation coefficient of 0.999. For  $(C_6H_5)_3 \text{SnSP}(0C_3H_7-i)_2$ between 77 and 155K the slope of  $-1.40 \times 10^{-2} \text{ K}^{-1}$  is based upon nine points with intercept at 1.075 and a correlation coefficient of 0.998. These slopes are within experimental error identical, and with the isomer shift (IS) and QS data specify that we are dealing here with very similar lattice dynamics in the two cases.

The more tightly bound the tin atoms are in a lattice, the slower the decrease in f, and hence  $A_T$ , is found as the temperature is raised. The slope of the plot of lnA vs. T is thus characteristic of the lattice packing of molecules. Non-interacting, monomeric molecules exhibit slopes of <u>ca</u>. -1.8x10<sup>-2</sup>K<sup>-1</sup> no matter what the coordination number at tin. A lattice held in part by weak intermolecular interactions such as hydrogen bonding reduces this value to <u>ca</u>. -1.7x10<sup>-2</sup>K<sup>-1</sup>. A more complex system of hydrogen bonds can further reduce the slope to <u>ca</u>. -1.3x10<sup>-2</sup>K<sup>-1</sup>. Lattices which are strongly hydrogen bonded or in which the tin atom participates in one-, two- or three dimensional association exhibit slopes of <u>ca</u>. -1.0x10<sup>-2</sup>K<sup>-1</sup> Tin(II) oxide exhibits the most gentle slope yet reported (-0.23x10<sup>-2</sup>K<sup>-1</sup>). <sup>37</sup>, <sup>38</sup> Against this background, the slope of <u>ca</u>. -1.40x10<sup>-2</sup>K<sup>-1</sup>

(5)

(6)

found for both the ethoxy and isopropoxy derivatives indicates a monomeric structure packed in a rather tight lattice. Comparison should be drawn with the corresponding slope data for tetraphenyltin,  $-1.659 \times 10^{-2} K^{-1}$ ,<sup>39</sup>,<sup>30</sup> for which a spectrum at ambient temperatures can be resolved.<sup>41</sup>

The effective vibrating mass model developed by Herber can be used to obtain the mass of the vibrating unit in the solid from the variation of the recoil-free fraction with temperature and the low energy ( $<200 \text{cm}^{-1}$ ) lattice mode absorptions in the Raman spectrum.<sup>42</sup>. The molecularity of the vibrating unit is calculated from:

$$M_{eff} = -\frac{3E_{\delta}^{2}k}{(hc)^{2}\omega_{L}^{2}}(\frac{dT}{dlnA})$$
(7)

where  $\frac{dlnA}{dT}$  is the slope of the plot of the normalized area under the Mössbauer resonance vs. temperature  $(-1.40 \times 10^{-2} \text{K}^{-1}$  for the compounds considered in Figure 1), and Ey is the energy of the Mössbauer gamma-ray. The low-energy Raman spectrum which should contain the lattice mode frequency  $\omega$  is shown in Figures 2 and 3 for the ethyl and isopropyl esters, while Table VI lists the correlation between the  $\omega$  frequencies and the M<sub>eff</sub> values. We are aware of no data in the literature which could serve as a guide for the assignment of the Raman-active bands below 50cm<sup>-1</sup>. The molecular weights of the ethyl and isoproyl ester monomers are 535 and 563, respectively. Thus no band in either spectrum above those found at 34 and 37 cm<sup>-1</sup>, respectively, can correspond to the unique intermolecular, intra-unit cell vibration sought in this treatment. These bands correspond to the monomer. None of the other Raman frequencies observed correspond to a reasonable integer unit above the monomer, thus ruling out structure C. This finding corroborates the Mössbauer IS and QS data which specify four coordination at tin which rules out structure B, and the magnitude of the slope of the plot of area vs. temperature which also rules out a polymeric lattice as Thus we are forced to conclude that the triphenyltin dithioin structure C. phosphate esters adopt a unique, monomeric, monodentate structure such as A.

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Table 1.	Irlorganoti	n Ditnio	pnospnate	Esters				
R3SnS2P(C	<u>R222</u>				<u>xc</u>		<u>ZH</u>	
R	<u>R'</u>	Prepa	Yield.%	mp/bp.°C.	<u>calcd</u>	found	calcd	found
C6H5	CH3 <sup>C</sup>	2,3	72	83°	6.12 <u>b</u>	6.00 <u>b</u>	1	
	с <sub>2</sub> н <sub>5</sub> <u>d</u>	2,3	89	105°	5.80 <u>b</u>	5.65 <u>b</u>		
	n-C <sub>3</sub> H <sub>7</sub> <sup>e</sup>	2,3	65	63°	5.51 <u>b</u>	5.40 <u>b</u>		
	1-C3H7	2,3	52	73.5-74.5°	51.16	51.01	5.20	5.27
	n-C4H9	2	94	68-9°	5.26 <sup>b</sup>	5.10 <sup>b</sup>		
	1-C4H9	1	63	52-54°	58.80	52.95	5.64	5.68
	с <sub>6</sub> н <sub>5</sub>	1	77	121°-122°	57.07	57.10	.4.00	4.17
CH3	СНЗ	3	25	<u>B</u>	18.71	20.34	4.71	5.08 <u>h</u>
	C2H5	1,3	64	112º115°/0.2	torr 24.09	23.89	5.49	5.41
· · · · ·	n-C3H7	3	75	oil				
	1-C3H7	3	75	105°-109°/ 0.4torr	28.67	28.73	6.15	6.28
C6H11	1-C3H7	4		43-44°				

8

Numbers 1,2 and 3 correspond to the syntheses described by Eqs. 1, 2 and 3; 4 was used as received from the Stauffer-Chemical Company. Its preparation was described in ref. 15 from the potassium salt of the acid (7.6g, 0.03 moles) and tricyclohexyltin chloride (10.1 g, 0.025 moles).

Analysis for phosphorus.

Ref. 3 reports a mp of 86°C.

Ref. 3 reports a mp of 105°; ref. 16 of 90°-91°C.

Ref 3 reports a mp of 63°C.

f

Ref. 3 reports a mp of 69.1°C.

This compound distilled over a wide temperature range, indicating some thermal decomposition. Purification could not be affected by gas chromatography. The composition is based upon n.m.r. and mass spectral data.

Molecular weight: calculated, 321; found (in benzene), 300.

Table II.	119m Sn	Mössbauer	Data	at	77K

	IS, mm/sª	QS, mm/s <sup>b</sup>	<u>r</u> 1mm/s <sup>c</sup>	r_mm/s <sup>d</sup>	ρ <sup>e</sup>
(C6H5)3SnS2P(OCH3)2	1.27	2.07	1.12	1.22	1.63
(C6H5)3SnS2P(OC2H5)2	1.26	2.08	1.10	1.24	1.65
$(C_6H_5)_3SnS_2P(OC_3H_7-i)_2$	1.28	2.03	1.09	1.23	1.59
$(C_6H_5)_3SnS_2P(OC_3H_7-n)_2$	1.26	2.03	1.08	1.22	1.61
$(C_6H_5)_3SnS_2P(0-C_4H_9-1)_2$	1.28	1.94	1.08	1.50	1.52
$(C_6H_5)_3SnS_2P(OC_6H_5)_2$	1.31	2.32	1.08	1.30	1.77
(CH <sub>3</sub> ) <sub>3</sub> SnS <sub>2</sub> P(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1.38	3.09	1.38	1.55	2.24
$(CH_3)_3 SnS_2^P(OC_3^{H_7-1})$	1.35	2.92	1.21	1.28	2.16
$(cyclo-C_6H_{11})_3SnS_2P(OC_3H_7-i)_2$	1.52	2.56	1.08	1.32	1.68

<u>a</u> <u>+0.02<sup>mm</sup>/s.</u> <u>b</u> <u>+0.03 <sup>mm</sup>/s.</u>

C High velocity resonance, ±0.04 mm/s. d Low velocity resonance, ±0.05 mm/s. e QS/IS.

R=C6H5;	R'=CH3	C2H5	n-C3H7	1-C3H7	1-C4H9	C6H5	
		3065w					
		2995					
		2990					
		293500					
		2900					
		2370vw					
						1592sh	
						1587m	
				1575vw	1574vw	1575w	
		1485m				1484vs	
		1445vw					
		1433s			1428m	1429s	
		1390m					
						1364vw	
						1350vw	•
	1328w	1336w		1328vw	1330vw	1330w	
	1295w	1310w	1295w	1295w	1295w	1300w	
				1254vw		1261vw	
						1240w	
						1199s	••
				1185sh	1185vw	1190m	
				1174m		1178vs	
•				1155w	1155w(br)	•	
	1166m	1160m	1145m(br)	1135m	1124w	1157vs	v((P)-0-C)ª
				1095m			
	1154sh	1102w					
		1095w					
	1065m	1075s	1069s	1069m	1070m	1060	
		1044s (br	)1048m(br)	1060sh	1046sh	100000	
			1015sh	1018vw	1019w	1022m	
			1000sh		001	1004m	W(P-0-(C))
	1007vs	1015vs	990s	990vs	9915	992m(1)	V(I -0-(C))
	990s	998s				0.91	
				9/0sh		965w	
		956vs	967s(br)	90505	ADAM	033ve	
		9358		932sn	000.	012ve	
•		924sh	906vw		900w	901e	
				002-		894vs	
				8030	860-	858	
			000-	0/.6	850m	0,000	
			832m	840VW	81 8m	825w(hr)	
	8098	805w	8100		OTOAM		
	794sh	796sh					
		790s				775va	
		770m					

s

cm

Table III. (continued)

			767s		76498	
		748s			747m	
	740s		741w		7375	
722vs	732s	722s	723s	723s	7298	
					720sh	
	700s		691s	692s	695s	
					689m	
633s(br)	655vs	655m	663s	655s	675vs	v (PS_)
					660w	asym 2
		639m	648sh		648vw	
					610vw	
106-				545w(br)	564m	
4801	540m	514m(br)	505s	521m	525s	V (PS2)
	515w					•)= -
422-		105	480w		489m	
43210	440m	4355	435s	437m	437s	
R	= CH <sub>3</sub> ;	$R' = CH_3$	C <sub>2</sub> H <sub>5</sub>	1-C3H7	$R = C_6 H_1$	$; R' = i - C_2 H_2$
						<u> </u>
		2985m	2990vs	29758		
		2940s	2940m	2930m		
		2910m	2910m	2920sh		
		2920m	2880w	2870		
			2780vw			
		1460sh	1480m			
		1452m	1455sh	1462m		
		1438m	1446m	1447m	14428	
			1393s	1381s	1370m	
			1370sh	1370s	1362sh	
				1348w	1349w	
					1340vw	
					1325vw	
			1294m (br)		1292w	
			1268vw		1263w	
			1190w			
					1175sh	
		1170-		1175m	1168m	_
		11/38	11645	1138m	1137m	$v((P)-0-C)^{\underline{a}}$
	•		1100	1102s	1103s	
			1100s			
					1080w	
		1040eb	1045		10000	
		1018 me (hr)	104575	0.95	1038w	
		2020000(01)	055wo (h-)	96378	96/VS	V(P-0-(C))
			JJVS(DI)	902VS(DT)	90505	
				9935	905W	
				0038	835	
					800	1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 -
		780vs(br)	788ve (h-)	785eb	0000	
			/00/8(01)	76500	768-	p(3n-C)
				10340	1008	

.

.

# Table III. (continued)

745s 700s 685sh	730sh 675sh	750sh	752w 719vw	
655vs	658ve	0000	665m	
530s	540	645s	650s	V (PS)
510sh	JAOVS	538s		asym 2
4955	5085	503m	541m	asym (Sn-C) sym (PS2)
			512w	sym (Sn-C)
390w	200.		480w	
	3000	380w		v(Sn-S)

asee Ref. 32.

G	CH 3	. 3	C6H5	C <sub>6</sub> H <sub>5</sub>	C6H5	с <sub>6</sub> н <sub>5</sub>	с <sub>6</sub> 1,5	C6H5	70
CH(CH <sub>3</sub> ) <sub>2</sub>	CH2 CH3	CH <sub>3</sub>	с <sub>6</sub> н <sub>5</sub>	сн <sub>2</sub> сн (сн <sub>3</sub> )	CH(CH <sub>3</sub> ) <sub>2</sub>	сн <sub>2</sub> сн <sub>2</sub> сн <sub>3</sub>	cli2cli3	сн <sub>3</sub>	
			7.0-8.2m (25)	2 7.23-7.93m (J	7.12-7.87 (15)	7.2-7.8m (15)	7.2-7.8m (15)	7.1-7.8m(15)	(c <sub>ó</sub> H <sub>5</sub> ) <sub>3</sub> sn <sup>a</sup>
0.68s()   <sup>2</sup> J( <sup>119</sup> Sn-C- <sup>1</sup> H) =	0.68s(9)   <sup>2</sup> J( <sup>119</sup> Sn-C- <sup>1</sup> H) =	0.66s(9)   <sup>2</sup> J( <sup>119</sup> Sn-С-'Н)		15)				8	(CH <sub>3</sub> ) <sub>3</sub> Sn <sup>ª</sup>
57.5	57.5	- 57.0		2 F	IIB PACE IS B ROM COPY DUR	IST QUALLITY NISHED TO DA	PRACIAL		(c <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> Sm <sup>ª</sup>
4.83m(2)   <sup>3</sup> J( <sup>31</sup> P-O-C-H) = 13.(   <sup>3</sup> J( <sup>1</sup> H-C-C- <sup>1</sup> H) =6.5	4.16m (4)   <sup>3</sup> J( <sup>31</sup> P-O-C- <sup>1</sup> H) = 10   <sup>3</sup> J( <sup>1</sup> H-C-C- <sup>1</sup> H) = 7.5	3.65d(6)   <sup>3</sup> J( <sup>31</sup> Р-0-С- <sup>1</sup> н) = 15		$3.64m(4)$ $ ^{3}J(^{31}P-0-C-^{1}H)  = 9$ $ ^{3}J(^{1}H-C-C-^{1}H)  = 6.5$	$ {}^{3}J({}^{3}H^{-}C-C^{-}H) ^{-}$ 12 $ {}^{3}J({}^{1}H-C-C^{-}H) ^{-}$ 6.0	$ {}^{3}J({}^{3}{}^{79t}(4)_{P-0-C-1}_{H} = 9.5$ $ {}^{3}J({}^{1}_{H-C-C-1}_{H}) = 6.5$	$ {}^{3}_{J}({}^{3}_{P-0-C-}^{3-91dq})  = 10.$ $ {}^{3}_{J}({}^{1}_{H-C-C-}^{1}_{H})  = 7.0$	$ {}^{3}J({}^{3}H^{+}P^{+}O^{-}C^{-}H^{+}) = 15.$	H <mark>a, b</mark>
1.36d(12) )   <sup>3</sup> J( <sup>1</sup> н-с-с- <sup>1</sup> н) = 6.5	1.36t(6) .0   <sup>3</sup> J( <sup>1</sup> H-C-C- <sup>1</sup> H) = 7.5	.0		1,4-2,0m(2) <sup>d</sup> 0.79 .0   <sup>3</sup> J( <sup>1</sup> H+C+C- <sup>1</sup> H) -	.0   <sup>3</sup> J( <sup>1</sup> H-C-C- <sup>1</sup> H) = 6.0	0.7–1.7m(10) <sup>c,d</sup>   <sup>3</sup> J( <sup>1</sup> H-C-C- <sup>1</sup> H)=6.0	0 <sup>1</sup> .99t( <sup>6</sup> ) 0 <sup>3</sup>   <sup>3</sup> ( <sup>31</sup> P-O-C- <sup>1</sup> H)  = 7.0	5	H <sub>g</sub> <sup>-42</sup> H <sub>g</sub> <sup>-,b</sup>

Spect	<u>C</u> Both <u>d</u> Satel	<u></u> <sup>b</sup> H <sub>α</sub> , β,	<sup>a</sup> Shift s=sin CDC1 <sub>3</sub>		с <sub>6</sub> н <sub>11</sub>	CH	R	Table IV.
rum recorded	H <sub>G</sub> and H <sub>B</sub> . lites unreso	γ refer to R	s in ppm; con glet; d=doub; solutions, u	•	CH(CH <sub>3</sub> ) <sub>2</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	R	(cont inued)
as a dilute soluti	lvable.	$_{3}$ sns <sub>2</sub> p[0(CH <sub>a</sub> ) <sub>x</sub> (CH <sub>b</sub> )	upling constants ir let; t=triplet; m=n unless otherwise ir				(c <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> sn <sup>a</sup>	
lon in pyridine.		<sub>y</sub> (CH ک <sup>ا</sup> تا ک	n Hz; the number of nultiplet; dq=double ndicated.			1.00s(9)   <sup>2</sup> J( <sup>119</sup> Sn-C-'Н) -	(CH <sub>3</sub> ) <sub>3</sub> Sn <sup>ª</sup>	•
			protons in resonand t of quartets. Al:		1.00-2.50m(33)	70.0	(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> Sn <sup>4</sup>	
			ce is given in pare l spectra are recor	<sup>3</sup> J( <sup>1</sup> H-C-C- <sup>1</sup> H) = (	<sup>d</sup> 4.93m(2)   <sup>3</sup> J( <sup>31</sup> P-0-C- <sup>1</sup> H) =	5.02m(2)   <sup>3</sup> J( <sup>31</sup> P-0-c- <sup>1</sup> H) =   <sup>3</sup> J('H-C-c- <sup>1</sup> H) = (	H <sub>α</sub> ā, b	
			ntlieses; ded as	5.0	1.28d(12) 12.0   <sup>3</sup> J( <sup>1</sup> H-C-C- <sup>1</sup> H	1.38d(12) 13.0  <sup>3</sup> J('н-с-с-'н) 5.5	H <sup>β</sup> ā•₽	
•••			•		) - 6.0	= 6.5	H.a.b	

Table	v.	Mass	Spectral	Data	for	(CH_)	SnS_P	(OR)
							_	

Physics and Article Street of the

$\underline{\mathbf{R}=1-\mathbf{C}_{3}\mathbf{H}_{7}}$	Mass Number	Rel. Abund.	Assignment
	363	29.7	(CH <sub>3</sub> ) <sub>2</sub> SnS <sub>2</sub> P(OC <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> +
•	321	21.9	(CH <sub>3</sub> ) <sub>2</sub> SnS <sub>2</sub> P(OH)(OC <sub>3</sub> H <sub>7</sub> ) <sup>+</sup>
	279	100.0	(CH <sub>3</sub> ) <sub>2</sub> SnS <sub>2</sub> P(OH) <sub>2</sub> +
	261	14.2	(CH <sub>3</sub> ) <sub>2</sub> SnS <sub>2</sub> P0 <sup>+</sup>
•	249	10.7	sns <sub>2</sub> <sup>P</sup> (OH) <sub>2</sub> <sup>+</sup>
	245	19.6	$(CH_3)_2 SnSPO_2^+ (or (CH_3)_2 SnS_2 P^+)$
•	214	12.2	HS2P(OC3H7)2 ?
	183	43.0	(CH <sub>3</sub> ) <sub>2</sub> SnSH <sup>+</sup>
	165	47.5	(CH <sub>3</sub> ) <sub>3</sub> Sn <sup>+</sup>
1.	153	19.8	SnSH <sup>+</sup>
	150	15.0	(CH <sub>3</sub> ) <sub>2</sub> Sn <sup>+</sup>
	135	24.2	(CH <sub>3</sub> )Sn <sup>+</sup>
$\frac{\mathbf{R} = C_2 H_5}{\mathbf{R} + C_2 H_5}$			<u> </u>
	335	97.2	$(CH_3)_2 SnS_2 P(OC_2 H_5)_2^+$
	307	• 19.7 •	(CH <sub>3</sub> ) <sub>2</sub> SnS <sub>2</sub> P(OH)OC <sub>2</sub> H <sub>5</sub> ) <sup>+</sup>
	279	63.0	(CH <sub>3</sub> ) <sub>2</sub> SnS <sub>2</sub> P(OH) <sub>2</sub> +
	261	27.2	(CH <sub>3</sub> ) <sub>2</sub> SnS <sub>2</sub> P0 <sup>+</sup>
	249	13.1	SnS <sub>2</sub> P(OH) <sub>2</sub> +
	245	. 29.3	(CH <sub>3</sub> ) <sub>2</sub> SnSPO <sub>2</sub> <sup>+</sup> (or (CH <sub>3</sub> ) <sub>2</sub> SnS <sub>2</sub> P <sup>+</sup> )
	229	14.5	(CH <sub>3</sub> ) <sub>2</sub> SnSP0 <sup>+</sup>
	214	21.7	2
•	211	28.6	?
	185	95.1	SnS <sub>2</sub> H <sup>+</sup> or SnPSH <sub>2</sub> <sup>+</sup>
	165	100.0	(CH <sub>3</sub> ) <sub>3</sub> Sn <sup>+</sup>
	148-157		overlapping clusters

44.3

Table V. (c	continued)		
	135	61.7	(CH <sub>3</sub> )Sn <sup>+</sup>
	121	33.8	(CH <sub>3</sub> )Sn <sup>+</sup>
	120	23.7	sn <sup>+</sup>
R = CH <sub>3</sub>	307	47.5	(CH <sub>3</sub> ) <sub>2</sub> SnS <sub>2</sub> P(OCH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>
	277	39.0	sns <sub>2</sub> P(OCH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>
	209-212	12.0-20.0	overlapping clusters
	200	32.7	? (no Sn)
	197	45.8	$(CH_3)Sn(OCH_3)_2^+$ or $(CH_3)SnP(OCH_2)^+$
	185	99.0	sns <sub>2</sub> H <sup>+</sup>
	172	40.0	?
	165	100.0	(CH <sub>3</sub> ) <sub>3</sub> Sn <sup>+</sup>
	146-155	13.0-40.6	overlapping clusters
	135	58.6	(CH <sub>3</sub> )Sn <sup>+</sup>
	125	47.3	?
	121	22.1	SnH <sup>+</sup>
	120	28.9	sn <sup>+</sup>

<sup>a</sup>Represents most intense peak for clusters containing tin, based on  $120_{Sn}$ ,  $32_{S}$ ,  $16_{O}$ ,  $12_{C}$ ,  $1_{H}$ ,  $31_{P}$ .

Addie VI. The Effective V.	torating Mas	ss Model.	Low Energy Latt	ice Mode	Rama
Frequencies and Moff Value	as.				
			Molecular		
S	۵	Meff	Weight Multiple		
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnSP(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	22	1487	2.78		
	34	623	1.16		
S "					
$(C_6H_5)_3$ snsp $(OC_3H_7-1)_2$	23	1390	2.47		
	33	675	1.20		
	37	.537	0.954		
	50	294	0.522		

Table VI The FFF. an

#### Figure Captions

Figure 1. The plot of lnA (normalized to the area under the resonance curve at  $77K_{2}vs_{1}$  temperature in K. The slopes are  $-1.43x10^{-2}K^{-1}$  for the ethyl and  $-1.40x10^{-2}K^{-1}$  for the isopropyl ester.

Figure 2. The low-energy, lattice-mode Raman spectrum of 0,0-diethyldithiophosphatotriphenyltin.

Figure 3. The low-energy, lattice-mode Raman spectrum of 0,0<sup>L</sup>-di-iso-propyldithio-phosphatotriphenyltin, (a)  $\lambda_0$ =4880 @ 100 mw, (b) $\lambda_0$ =5145 @ 200 mw.

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 $Ph_3SnS_2P(0iPr)_2$ 88 76 64 52 40 S = laser line 3 28 16 (cm<sup>-1</sup>) (a)