Synthesis and Vibrational and Mass Spectra of (n-Bu)2Sn(O2PMe2)2, (n-Bu)2Sn(O2PMcPh)2 and (n-Bu)2Sn(O2PPh2)2

Abdel-Fattah Shihada
Department of Chemistry, Faculty of Science, U.A.E. University, Al-Ain, P.O. Box: 17551, United Arab Emirates

Z. Naturforsch. 50b, 745–749 (1995); received November 10, 1994

IR Spectra, Raman Spectra, Mass Spectra, Di-n-butyltin Dimethylphosphinate

Di-n-butyltin dimethylphosphinate has been synthesized by the reaction of (n-Bu)2Sn(OOCCH3)2 with HO2PMe2 in benzene. The reactions of (n-Bu)2Sn(OOCCH3)2 with MePhP0Cl and Ph3P0Cl in toluene have been used to prepare (n-Bu)2Sn(O2PMePh)2 and (n-Bu)2Sn(O2PPh2)2, respectively. On the basis of vibrational spectra and physical properties it is concluded that the title compounds are polymerized and the ligands function as O–P–O bridges between the tin atoms. The n-butyl groups are in trans position in the resulting octahedral environment around tin. Loss of n-butyl radicals and of the diorganophosphinate group from tin represent the main fragmentation processes in the EI mass spectra of (n-Bu)2Sn(O2PRR′)2 (RR′ = Me2, MePh, Ph2). The mass spectra show Sn(O2PRR′)2 as the base peak.

Introduction

The reactions of organotin oxides with phosphoryl halides (POX3; X = Cl, Br) [1, 2] and with organophosphoryl chlorides (R2POCl) [3] have been used in the synthesis of organotin dihalophosphinate and organotin diorganophosphinates respectively. These compounds are generally assigned a polymeric structure with tin atoms joined by O–P–O bridges. The polymeric structures of Me3SnO2PCl2 and Me2SnO2PMe2 [4] have been confirmed by X-ray diffraction methods. Recently we have studied the synthesis, vibrational spectra and mass spectra of P2SnO2PRR′ compounds (RR′ = Me2, MePh, Ph2) [3]. We report here the reactions of (n-Bu)2Sn(OOCCH3)2 with Ph3POCl and with MePhP0Cl and the synthesis of (n-Bu)2Sn(O2PPh2)2 (RR′ = Me2, MePh, Ph2). The vibrational spectra and the mass spectra of the prepared compounds are assigned and discussed.

Results and Discussion

Di-n-butyltin acetate reacts with phosphinic chlorides PR′POCl (RR′ = MePh, Ph2) in toluene at room temperature to give products of the type (n-Bu)2Sn(O2PRR′)2 according to the following equation.

\[(n-Bu)2Sn(OOCCH3)2 + 2 RR′POCl \rightarrow (n-Bu)2Sn(O2P RR′)2 + 2 CH3COCl\]

Anhydrous metal acetates react with POCl3 to produce metal dichlorophosphates along with CH3COCl [5, 6]. Me3Si02PBr2 was prepared by the reaction of POBr3 with Me3SiOCOCH3 [7].

Relatively low yield is obtained when RR′POCl is added to (n-Bu)2Sn(OOCCH3)2 in 2:1 molar proportions. No significant change of the yield results if the reactions are carried out in toluene or diethyl ether, or without solvent. On the other hand, the reactions of RR′POCl compounds with an excess of (n-Bu)2Sn(OOCCH3)2 in toluene lead to the formation of (n-Bu)2Sn(O2PRR′)2 products in high yield. Consequently, the low yield may due to the reaction of (n-Bu)2Sn(O2PRR′)2 with RR′POCl to give (n-Bu)2SnCl2 according to the following reaction.

\[(n-Bu)2Sn(O2P RR′)2 + 2 RR′POCl \rightarrow (n-Bu)2SnCl2 + 2 (RR′PO)2O\]

In this connection, it is worth noting that the formation of CuCl2 as a side product has been observed by the reaction of Cu(OOCCH3)2 with POCl3 [6]. The synthesis of (n-Bu)2Sn(O2PPh2)2 by the reaction of (n-Bu)2SnCl2 with NaO2PPh2 [8] or NH2O2PPh2 [9] has been reported. (n-Bu)2Sn(O2PMe2)2 is prepared by the reaction of (n-Bu)2Sn(OOCCH3)2 with Me2PO3H in benzene.

0932–0776/95/0500–0745 $06.00 © 1995 Verlag der Zeitschrift für Naturforschung. All rights reserved.
Table I. IR and Raman spectra (1300−1000 cm\(^{-1}\)) of (\(n\)-Bu)\(_2\)Sn(O\(_2\)PMe\(_2\))\(_2\), (\(n\)-Bu)\(_2\)Sn(O\(_2\)PMePh\(_2\))\(_2\) and (\(n\)-Bu)\(_2\)Sn(O\(_2\)PPh\(_2\))\(_2\).

<table>
<thead>
<tr>
<th>((n\text{-}Bu)\text{Sn}(O\text{2}PMe(_2))(_2)</th>
<th>((n\text{-}Bu)\text{Sn}(O\text{2}PMePh(_2))(_2)</th>
<th>((n\text{-}Bu)\text{Sn}(O\text{2}PPh(_2))(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR</td>
<td>Raman</td>
<td>IR</td>
</tr>
<tr>
<td>------</td>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>1296 s</td>
<td>1287 w</td>
<td>1297 m</td>
</tr>
<tr>
<td>1264 vw</td>
<td>1246 vw</td>
<td></td>
</tr>
<tr>
<td>1186 sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1161 sh</td>
<td>1165 s−vs</td>
<td>1165 sh</td>
</tr>
<tr>
<td>1146 sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1107 vs</td>
<td>1090 w−m</td>
<td>1132 vs</td>
</tr>
<tr>
<td>1083 w−m</td>
<td>1085 w</td>
<td>1076 s</td>
</tr>
<tr>
<td>1051 sh</td>
<td>1056 s</td>
<td>1042 m−s</td>
</tr>
<tr>
<td>1031 s−vs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1017 s</td>
<td>1021 sh</td>
<td>1022 m−s</td>
</tr>
<tr>
<td>998 w</td>
<td>1000 vs</td>
<td>999 w</td>
</tr>
<tr>
<td>974 sh</td>
<td>973 vw</td>
<td>970 vw</td>
</tr>
<tr>
<td>924 m</td>
<td>927 w</td>
<td>920 vw</td>
</tr>
<tr>
<td>889 w−m</td>
<td>883 w</td>
<td>884 vw</td>
</tr>
<tr>
<td>874 s</td>
<td>879 sh</td>
<td>878 s</td>
</tr>
<tr>
<td>864 vw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>853 w</td>
<td>852 w</td>
<td>852 w</td>
</tr>
<tr>
<td>772 vw</td>
<td>776 vw</td>
<td>771 w−m</td>
</tr>
<tr>
<td>745 m</td>
<td>745 w−m</td>
<td>737 s−vs</td>
</tr>
<tr>
<td>721 sh</td>
<td>722 vw</td>
<td></td>
</tr>
<tr>
<td>707 m</td>
<td>708 s</td>
<td></td>
</tr>
<tr>
<td>687 m−s</td>
<td>693 s</td>
<td>699 s</td>
</tr>
<tr>
<td>627 w−m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600 vw</td>
<td>595 vs</td>
<td>620 s</td>
</tr>
<tr>
<td></td>
<td>602 s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>521 s</td>
<td>518 w</td>
</tr>
<tr>
<td>492 s</td>
<td>493 s</td>
<td>486 m−s</td>
</tr>
<tr>
<td>432 w−m</td>
<td>418 w</td>
<td>401 vw</td>
</tr>
<tr>
<td>401 vw</td>
<td>370 vw</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>396 w</td>
<td>390 w</td>
<td>390 w</td>
</tr>
<tr>
<td>348 vw</td>
<td>353 vw</td>
<td>359 w</td>
</tr>
<tr>
<td>309 w</td>
<td>307 w</td>
<td>312 m</td>
</tr>
<tr>
<td>296 vw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>237 m</td>
<td>277 w</td>
<td>273 w</td>
</tr>
<tr>
<td>219 w</td>
<td>226 m</td>
<td>221 vw</td>
</tr>
<tr>
<td>213 sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>187 vw</td>
<td>189 vw</td>
<td>192 w</td>
</tr>
<tr>
<td>162 vw</td>
<td>177 w</td>
<td></td>
</tr>
<tr>
<td>144 w−m</td>
<td>136 w</td>
<td>145 m−s</td>
</tr>
</tbody>
</table>
Vibrational spectra

Table I lists the observed infrared and Raman frequencies of \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PRR'})_2\) \((\text{RR'} = \text{Me}_2, \text{MePh}, \text{Ph}_2)\), with the relative intensities and assignments. The frequencies of the \(\text{O}_2\text{PRR'}\) group were assigned by comparison with the vibrational spectra of \(\text{Ph}_3\text{SnO}_2\text{PRR'}\) [3]. The appearance of \(\nu(\text{PO}_2)\) frequencies between 1200 and 1000 cm\(^{-1}\) is consistent with bidentate bonded \(\text{O}_2\text{PRR'}\) groups. Monodentately bonded \(\text{O}_2\text{PRR'}\) group shows frequencies \(\nu(\text{P}=\text{O}) > 1200 \text{ cm}^{-1}\) and \(\nu(\text{P}-\text{O}) < 1000 \text{ cm}^{-1}\). This behaviour and the physical properties such as involatility and insolubility in common organic solvents indicate polymeric structures of \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PRR'})_2\) in which the tin atoms are hexa-coordinated and linked by double \(\text{O}-\text{P}-\text{O}\) bridges. As a result of such bridges, \(\text{Sn}_2 \text{O}_4 \text{P}_2\) eight-membered rings are likely to be formed.

As observed earlier in the vibrational spectra of \(\text{Ph}_3\text{SnO}_2\text{PRR'}\) [3], the \(\nu_{as}(\text{PO}_2)\) frequency of \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PRR'})_2\) decreases in the transition from \(\text{RR'} = \text{Ph}_2\) to \(\text{RR'} = \text{MePh}\) to \(\text{RR'} = \text{Me}_2\) as a result of decreasing electron withdrawing power of \(\text{RR'}\) in the same direction. The Raman spectra of \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PMePh})_2\) and \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PPh}_2)_2\) display bands at 620 cm\(^{-1}\) assignable to \((\text{C}-\text{C}-\text{C})\) bending of the phenyl groups. Corresponding modes are observed at 618–621 cm\(^{-1}\) in the vibrational spectra of \(\text{Ph}_3\text{SnO}_2\text{PRR'}\) [3]. The absence of this band in the vibrational spectra of \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PMe}_2)_2\) supports the given assignment. The Raman spectra of \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PMePh})_2\) and \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PPh}_2)_2\) show the characteristic very strong band due to phenyl ring breathing at 1000 and 1001 cm\(^{-1}\), respectively.

Structural information concerning the \(\text{SnC}_2\) geometry can be obtained from the \(\nu(\text{SnC}_2)\) frequencies. For a linear \(\text{CSnC}\) arrangement \(\nu_{as}(\text{SnC}_2)\) will be infrared active, but Raman inactive, and vice versa for the \(\nu(\text{SnC}_2)\) vibration. Pertinent bands at 627, 634 and 638 cm\(^{-1}\) appear only in the IR spectra of \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PMe}_2)_2\), \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PMePh})_2\) and \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PPh}_2)_2\), respectively, and are attributed to \(\nu_{as}(\text{SnC}_2)\) vibrations. The \(\nu_{as}(\text{SnC}_2)\) vibrations were assigned at 644 and 645 cm\(^{-1}\) in the IR spectra of \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PF}_2)_2\) [10] and \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PH}_2)_2\) [11], respectively. The very strong Raman band at 595 cm\(^{-1}\) for \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PMe}_2)_2\) and the strong Raman bands at 602 cm\(^{-1}\) for \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PMePh})_2\) and 603 cm\(^{-1}\) for \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PPh}_2)_2\) are ascribed to \(\nu(\text{SnC}_2)\) vibrations. Corresponding \(\nu(\text{SnC}_2)\) absorptions are absent in the IR spectra of \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PMePh})_2\) and \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PPh}_2)_2\). Accordingly, the \(\nu(\text{SnC}_2)\) frequencies are consistent with a linear \(\text{CSnC}\) arrangement for \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PMe}_2)_2\) and \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PMePh})_2\). The appearance of \(\nu(\text{SnC}_2)\) as a very weak band at 600 cm\(^{-1}\) in the IR spectrum of \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PMe}_2)_2\) may indicate a deviation from \(\text{CSnC}\) linearity. Consequently, a sheet-like polymeric structure for \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PMe}_2)_2\) can be suggested with the butyl groups in a \textit{trans}-octahedral position. Similar structures have been found in \(\text{Me}_2\text{Sn}(\text{O}_2\text{PCl}_2)_2\) [12], \(\text{Et}_2\text{Sn}(\text{O}_2\text{PCl}_2)_2\) [1], \(\text{R}_2\text{Sn}(\text{O}_2\text{PF}_2)_2\) [10] and \(\text{R}_2\text{Sn}(\text{O}_2\text{PH}_2)_2\) [11] \((\text{R} = \text{Me}, \text{Et}, \text{n-Bu})\).

A polymeric structure with hexa-coordinated tin atoms has been proposed for \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PPh}_2)_2\) on the basis of \(^{119}\text{Sn}\) Mößbauer spectra [13].

Mass spectra

Table II gives the intensities of characteristic peaks in the EI mass spectra \((70 \text{ eV})\) of \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PRR'})_2\) \((\text{R} = \text{R'} = \text{Me, Ph}; \text{R} = \text{Me}, \text{R'} = \text{Ph})\). The molecular ion \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PRR'})_2^+\) is absent but the mass spectra of \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PMe}_2)_2\) and \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PMePh})_2\) show the molecular ion minus a methyl group with low abundance.

Fragments with masses greater than the molecular mass of the monomer appear in the mass spectra of \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PRR'})_2\), which is in agreement with the polymeric structure of the compounds. The \(\text{Sn}(\text{O}_2\text{PRR'})^+\) ion represents the base peak in the spectra of \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PRR'})_2\), while the spectra of \(\text{Ph}_3\text{SnO}_2\text{PRR'}\) [3] show \(\text{Ph}_2\text{SnO}_2\text{PRR'}^+\) as the base peak. Consistent with previous observations for \(\text{Ph}_3\text{SnO}_2\text{PRR'}\) [3], the loss of \(\text{n-butyl}\) radicals and of the entire \(\text{O}_2\text{PRR'}\) group from tin represent the major fragmentation processes of \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PRR'})_2\).

Noteworthy is the occurrence of \(\text{PhSn}^+\) ion in the mass spectra of \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PMePh})_2\) \((38\%)\) and \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PPh}_2)_2\) \((28\%)\) indicating a phenyl group transfer and the greater strength of the \(\text{Sn}–\text{Ph}\) bond as compared with Sn-Alkyl bonds.

The mass spectra of \((\text{n-Bu})_2\text{Sn}(\text{O}_2\text{PRR'})_2\) exhibit the even electron ions \(\text{BuSn}(\text{O}_2\text{PRR'})^2_2\),
R = R' = Me  R = Me, R' = Ph  R = R' = Ph

<table>
<thead>
<tr>
<th>Ionic Species</th>
<th>m/e (relative intensity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO₂RBU₂Sn(O₂PMe₂)²⁺</td>
<td>-</td>
</tr>
<tr>
<td>HO₂BU₂Sn(O₂PMe₂)²⁺</td>
<td>453(0.5)</td>
</tr>
<tr>
<td>Bu₂Sn(O₂PMe₂)⁺</td>
<td>405(1)</td>
</tr>
<tr>
<td>BuSn(O₂PR')₂</td>
<td>363(49)</td>
</tr>
<tr>
<td>HSn(O₂PR')²⁺</td>
<td>307(20)</td>
</tr>
<tr>
<td>Sn(O₂PR')²⁺/O₂PR⁺</td>
<td>291(6)</td>
</tr>
<tr>
<td>Bu₂Sn(O₂PR')⁺</td>
<td>327(14)</td>
</tr>
<tr>
<td>Sn(O₂PR')⁺</td>
<td>213(100)</td>
</tr>
<tr>
<td>SnO₂⁺</td>
<td>183(2)</td>
</tr>
<tr>
<td>SnR'²⁺</td>
<td>135(7)</td>
</tr>
<tr>
<td>HO₂PR'⁺</td>
<td>94(4)</td>
</tr>
<tr>
<td>O₂PR⁺</td>
<td>-</td>
</tr>
<tr>
<td>HO₂PR⁺</td>
<td>79(10)</td>
</tr>
</tbody>
</table>

Table II. Characteristic ions formed in the 70 eV mass spectra of (n-Bu)₂Sn(O₂PMe₂)₂, (n-Bu)₂Sn(O₂PMePh)₂, and (n-Bu)₂Sn(O₂PPPh₂)₂ (m/e (%)).

H₂Sn(O₂PR')²⁺ and Bu₂Sn(O₂PR')⁺ in considerable abundance.

The appearance of even electron tin-containing fragments with significant intensity is very common in the mass spectra of organotin compounds [14, 15].

Experimental

The IR spectra were obtained with a Bruker instrument IFS 88 equipped with KBr and polyethylene windows; Nujol mulls were used. The Raman spectra were recorded with a Dilor XY multichannel system instrument with 514.5 nm excitation of 10–40 mW power. Mass spectra were recorded on a Varian MAT CH 7 A instrument (EI 70 eV). The elemental analyses were performed by the analytical laboratory of Fachbereich Chemie der Universität Marburg, Germany. The reactions of (n-Bu)₂Sn(OCOCH₃)₂ with Ph₂POCl and PhMePOCl were carried out under anhydrous conditions.

Preparation of (n-Bu)₂Sn(O₂PMe₂)₂

A solution of HO₂PMe₂ (0.2 g, 2.13 mmol in 15 ml benzene) was added to a solution of (n-Bu)₂Sn(OCOCH₃)₂ (0.39 g, 1.1 mmol) in 10 ml benzene at room temperature. After few minutes a white crystalline precipitate began to form. The reaction mixture was kept for 2 d at room temperature. The resulting precipitate of (n-Bu)₂Sn(O₂PMe₂)₂ was filtered off, washed with benzene, then with diethyl ether and dried in vacuum. The yield was 0.24 g (54%). (n-Bu)₂Sn(O₂PMe₂)₂ is insoluble in CCl₄, CH₂Cl₂, methanol and acetone; m.p. >200 °C.

Preparation of (n-Bu)₂Sn(O₂PPPh₂)₂

Ph₂POCl (0.67 g, 2.8 mmol) was added to a solution of (n-Bu)₂Sn(OCOCH₃)₂ (4.0 g, 11.4 mmol) in 20 ml toluene. The reaction mixture was kept for 2 d at room temperature. The precipitate of (n-Bu)₂Sn(O₂PPPh₂)₂ was filtered off, washed with toluene, then with diethyl ether and dried in vacuum. The yield was 0.92 g (97%). (n-Bu)₂Sn(O₂PPPh₂)₂ is insoluble in CCl₄, CH₂Cl₂, methanol and acetone; m.p. >200 °C.

Preparation of (n-Bu)₂Sn(O₂PMePh)₂

PhMePOCl reacts with an excess of (n-Bu)₂Sn(OCOCH₃)₂ in a procedure as described for (n-Bu)₂Sn(O₂PPPh₂)₂. The compound is insoluble in CCl₄, CH₂Cl₂, methanol and acetone; m.p. >200 °C.

Acknowledgements

I am grateful to Prof. Dr. K. Dehnicke (Fachbereich Chemie der Universität Marburg, Germany) for providing access to instrumentation facilities and to Prof. Dr. J. Weidlein (Institut für Anorganische Chemie der Universität Stuttgart, Germany) for assistance in recording the Raman spectra.