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STRUCTURAL STUDIES IN MAIN GROUP CHEMISTRY

XXV *. TIN DERIVATIVES OF *N*-ACYLHYDROXYLAMINES; FURTHER STUDIES

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Summary

The tin derivatives of *N*-acylhydroxylamines, $(CH_3)_2Sn[ON(CH_3)COCH_3]$, $R_2Sn[ON(Ph)COPh]_2$ (R = CH_3, Ph, n-C_4H_9, n-C_8H_{17}), n-$C_4H_9Sn[ON(Ph)COPh]_3$, $(CH_3)_3Sn[ON(Ph)SO_2C_6H_4CH_3]$, $X_2Sn[ON(E)COPh]_2$ (X = Cl, Br, I; E = H, Ph), $(CH_3)_2SnX[ON(Ph)COPh]$ (X = Cl, Br, I); $Cl_2Sn[ON(CH_3)COCH_3]_2$ have been prepared. The reaction of *N*-acetyl-*N*-methylhydroxylamine with hexamethyldisilazane yielded the trimethylsilyl hydrazine, $(CH_3)_3SiNH—N(CH_3)COCH_3$. From several attempted syntheses of triorganotin derivatives only products of disproportionation were isolated, In particular, $(CH_3)_3Sn[ON(CH_3)COCH_3]$, which could be isolated from the reaction of the hydroxylamine and $(CH_3)_3SnNEt_2$ in cold ether, disproportionated to $(CH_3)_2Sn[ON(CH_3)COCH_3]_2$ and $(CH_3)_4Sn$ in refluxing ether after 30 min or by heating the solid to ca. 70°C. Tin-119 Mössbauer, vibrational, and mass spectral data are reported for the derivatives and discussed in detail.

Introduction

In previous papers we have described the synthesis, spectroscopic properties, and structures of some triorganotin derivatives of *N*-acylhydroxylamines [1,2], as well as the structures of $Me_2Sn(ONMeCOMe)_2$ [3], $Me_2Sn(ONHCOMe)_2$ [4], $Me_2Sn(ONHCOMe)_2 \cdot H_2O$ [4] and $Cl_2Sn(ON(PhCOPh)_2$ [5]. In every case, the *N*-acylhydroxylamino ligand behaved as a bidentate chelating ligand towards tin, thus providing the first corroborated example of the five-coordinated *cis*-(R_3SnX_2) geometry ($Ph_3SnONPhCOPh$) [2], which as since also been demonstrated for $Me_3SnONPhCOPh$ [6]. $Me_2Sn(ONMeCOMe)_2$ exhibits a distorted octahedral geo-

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* For part XXIV see ref. 32.

metry at tin with a CSnC bond angle of 145.8(3)° [3], but the *N*-proto analogue, $Me_2Sn(ONHCOMe)_2$ is only little perturbed from the *cis*-octahedral geometry (CSnC = 109.1(4)°) due to the presence of NH···O=C hydrogen bonds. However, the corresponding monohydrate exhibits a similar stereochemistry to that of $Me_2Sn(ONMeCOMe)_2$ with a CSnC bond angle of 156.8(8)°, again due to a rather complex system of intermolecular hydrogen bonds [4]. $Cl_2Sn(ONPhCOPh)_2$ has the expected *cis*-octahedral geometry [5]. We have only briefly mentioned the spectroscopic properties of these derivatives before, and so in this paper we report details of the syntheses and spectroscopic data for them and several other *N*-acylhydroxylamino derivatives of tin.

Experimental

N-Benzoyl-*N*-phenylhydroxylamine (Hopkin and Williams), *N*-benzoylhydroxylamine (Eastman Kodak) and potassium hydroxamate (Koch-Light) were commercial products and used as obtained. *N*-4-Methylbenzoylhydroxylamine and *N*-acetylhydroxylamine were obtained by reaction of the appropriate acyl chloride and hydroxylamine hydrochloride as described by Jones and Hurd [7] for benzohydroxamic acid. The latter compound was extremely hygroscopic, and was stored under argon. *N*-Acetyl-*N*-methylhydroxylamine was prepared as follows: *N*-methylhydroxylamine hydrochloride was obtained by the reduction of nitromethane in an aqueous medium using ammonium chloride at zinc dust maintaining the temperature lower than 15°C, as described by Beckmann [8]. Reaction of the hydrochloride with acetyl chloride and NA_2CO_3 after the method of Ulrich and Sayigh [9] to give *N*-acetyl-*N*-methylhydroxylamine as a very pale yellow oil which contained some impurities.

Attempted purification by distillation in vacuo gave a product which remained contaminated (approximately 2—5% estimated from NMR measurements). Gas-liquid chromatography on several different columns at various temperatures (80—150°C) resulted in rearrangement to give three major components, which were not identified. The cleanest sample of $HON(CH_3)COCH_3$ was obtained by distillation in vacuo of a freshly prepared sample (fraction collected at 79°C/1.5 mmHg). Found: C, 39.10; H, 7.49; N, 15.69%. $C_3H_7O_2N$ calcd.: C, 40.44; H, 7.92; N, 15.72%. NMR data ($CDCl_3$ coln.) δ 2.12 ppm (CH_3-C), 3.24 (CH_3-N), 9.65 (OH).

N-Phenyl-*N*-tosylhydroxylamine was obtained from *N*-phenylhydroxylamine (by reduction of nitrobenzene with zinc dust and ammonium chloride in water) and *p*-toluenesulphonyl chloride as described by Shokol [10] and recrystallised from petrol (60—80)/benzene. Found: C, 58.97; H, 4.85; N, 5.16; S, 11.94. $C_{13}H_{13}O_3NS$ calcd.: C, 59.30; H, 4.98; N, 5.32; S, 12.18%.

Infrared spectra were recorded using a Perkin—Elmer 521 Spectrophotometer, Raman spectra using a Cary 81 instrument mass spectra using an AEI MS-902 instrument, and ^1H NMR data using a Varian HA-100 spectrometer. The Mössbauer data were filled to Lorentzian line shapes using usual least-squares methods.

Preparation of the organotin derivatives

(a) Dimethyltin bis-N-benzoyl-N-phenylhydroxylamine. $(CH_3)_2SnO$ (1.250 g; 7.59 mmol and HON(Ph)COPh (3.190 g; 14.96 mmol) were refluxed together

in benzene (70 ml) under a Dean and Stark water separator for 4 h. The cooled reaction mixture was filtered and a white solid was precipitated by addition of ether. The solid was removed and recrystallised from warm cyclohexane to give dimethyltin bis-*N*-benzoyl-*N*-phenylhydroxylamine (yield 3.52 g, 66.4%) as a creamy white microcrystalline solid (m.p. 155°C). Found: C, 58.37; H, 4.70; N, 4.75. $C_{28}H_{26}O_4N_2Sn$ calcd.: 58.67; H, 4.57; N, 4.89%. NMR data (CDCl$_3$ soln.): δ 0.78 ppm ((CH$_3$)$_2$Sn), 7.19 (Ph), $^2J(^{119,117}\text{Sn—C—}^1\text{H})$ 78.7, 75.0 Hz.

(b) Di-n-butyltin bis-N-benzoyl-N-phenylhydroxylamine. (n-C_4H_9)$_2$SnO (1.246 g; 5.01 mmol) and HON(Ph)COPh (2.132 g; 10.00 mmol) were reacted and extracted as in (a) giving di-n-butyltin bis-*N*-phenylhydroxylamine (yield 2.65 g; 80.6%), as a creamy white solid. Found: C, 62.01; H, 5.89; N, 3.90. $C_{34}H_{38}O_4N_2Sn$ calcd.: C, 62.20; H, 5.83; N, 4.27%. NMR data (CDCl$_3$ soln.): δ 7.11 ppm (Ph), complex butyl pattern.

(c) Di-n-octyltin bis-N-benzoyl-N-phenylhydroxylamine. (n-C_8H_{17})$_2$SnO (2.107 g; 5.83 mmol) and HON(Ph)COPh (1.597 g; 7.49 mmol) were reacted as in (a), although a thick brown oil was obtained on reducing the reaction volume after filtration. All attempts to obtain a solid product failed, and the attempted distillation in vacuo brought about degradation of the product. However, partition of the crude product between benzene and aqueous ethanol gave a pure sample of di-n-octyltin bis-*N*-benzoylphenylhydroxylamine, as a brown viscous oil. Found: C, 65.4; H, 7.38; 3.54. $C_{42}H_{54}O_4N_2Sn$ calcd.: C, 65.6; H, 7.07; N, 3.64%.

(d) Diphenyltin bis-N-benzoyl-N-phenylhydroxylamine. Ph$_2$SnO (0.963 g; 3.34 mmol) and HON(Ph)COPh (1.420 g; 6.66 mmol) were reacted and extracted as in (a) to give diphenyltin bis-*N*-benzoyl-*N*-phenylhydroxylamine (yield 1.06 g; 45.7%), as a creamy white solid. Found: C, 65.14; H, 4.63; N, 2.06. $C_{38}H_{30}O_4N_2Sn$ calcd.: C, 65.48; H, 4.34; N, 4.02%.

(e) n-butyltin tris-N-benzoyl-N-phenylhydroxylamine. (n-C_4H_9)SnO(OH) (1.045 g; 5.00 mmol) and HON(Ph)COPh (3.195 g; 14.98 mmol) were refluxed together in benzene (50 ml) under Dean and Stark conditions until no further water was removed. Evaporation of the reaction mixture and recrystallisation in pentane gave n-butyltin tris-*N*-benzoyl-*N*-phenylhydroxylamine (yield 2.23 g; 54.9%) as a yellow solid. Found: C, 63.24; H, 4.74; N, 4.62. $C_{43}H_{39}O_6N_3Sn$ calcd.: C, 63.60; H, 4.84; N, 5.17%. NMR data (CDCl$_3$ soln.) indicates expected integrated peak ratio 30 (Ph) : 9 (Bu).

(f) Attempted preparation of phenyltin tris-N-benzoyl-N-phenylhydroxylamine. Lithium metal (0.070 g; 1.01 mmol) was dissolved in a dry methanol (10 ml), and to this was added dropwise with stirring a solution of HON(Ph)COPh (2.132 g; 1.00 mmol) in dry methanol (8 ml). PhSnCl$_3$ (1.010 g; 3.34 mmol) in dry methanol (9 ml) was added to the above prepared solution, and the yellow solution became brown. On concentration a brown oil separated out, which was removed, washed with methanol and redissolved in a large volume of methanol. The solution was again concentrated, and the brown oil again removed, and dried in vacuo, whereupon a brown solid formed (m.p. 110°C) Found: C, 62.38; H, 4.87; N, 5.05. $C_{45}H_{35}O_6N_3Sn$ calcd.: C, 64.93; H, 4.24; N, 5.05%. Subsequent attempts to recrystallise the solid failed to improve the analysis.

(g) Attempted preparation of dichlorotin bis-N-benzoyl-N-phenylhydroxylamine. SnCl$_4$ · 5 H$_2$O (1.754 g; 5.00 mmol) in methanol (10 ml) was added drop-

wise with stirring to a methanol solution (30 ml) of HON(Ph)COPh (2.133 g; 10.00 mmol) with immediate formation of an intense violet colouration, which on standing became more intense. Attempts to isolate a single product failed.

(h) Attempted preparation of dibromotin bis-N-benzoyl-N-phenylhydroxylamine. Bromine (1.340 g; 8.38 mmol) in methanol (20 ml) was added dropwise with stirring to a solution of $(CH_3)_2$SnON(Ph)COPh$_2$ (2.400 g; 4.19 mmol) in methanol (40 ml). A green colouration was initially formed, which intensified on standing. Evaporation of the solution in vacuo, yielded an involatile red oil, from which individual products could not be isolated.

(i) Dichlorotin bis-N-benzoyl-N-phenylhydroxylamine. Lithium (0.074 g; 10.66 mmol) was dissolved in dry methanol (15 ml) and to this was added a solution of HON(Ph)COPh (2.133 g; 10.00 mmol) in dry methanol (15 ml). To this was added dropwise with stirring $SnCl_4$ (1.306 g; 5.012 mmol) also in dry methanol (10 ml), whereupon a white precipitate was formed, which was filtered off, washed with methanol and ether and dried in vacuo. (Yield of crude product 3.05 g; 99.3%.) The solid was recrystallised from a methanol/chloroform mixture to give dichlorotin bis-*N*-phenylhydroxylamine as a white crystalline solid (m.p. 180.5°C). Found: C, 50.71; H. 3.43; N, 4.46. $C_{26}H_{20}O_4N_2Cl_2Sn$ calcd.: C, 50.90; H, 3.31; N, 4.57%.

(j) Dibromotin bis-N-benzoyl-N-phenylhydroxylamine. Lithium (0.047 g; 6.77 mmol), HON(Ph)COPh (1.422 g; 6.67 mmol) and $SnBr_4$ (1.513 g; 3.45 mmol) were reacted and extracted as in (i), to give dibromotin bis-*N*-benzoyl-*N*-phenylhydroxylamine (yield: 1.77 g; 75.6%) as a slightly pink crystalline solid (m.p. 186°C). Found: C, 43.90; H, 2.95; N, 3.93. $C_{26}H_{20}O_4N_2Br_2Sn$ calcd.: C, 44.40; H, 2.89; N, 3.98%.

(k) Diiodotin bis-N-benzoyl-N-phenylhydroxylamine. Lithium (0.053 g; 7.59 mmol, HON(Ph)COPh (1.422 g; 6.67 mmol) and freshly recrystallised SnI_4 (2.088 g; 3.33 mmol) were reacted and extracted as in (i) to give diiodotin bis-*N*-benzoyl-*N*-phenylhydroxylamine (yield: 1.35 g; 5.07%) as a white crystalline solid. Found: C, 39.58; H, 2.63; N, 3.74. $C_{26}H_{20}O_4N_2I_2Sn$ calcd.: C, 39.18; H, 2.53; N, 3.51%.

(l) The reaction of anhydrous tin(IV) chloride and N-benzoyl-N-phenylhydroxylamine. HON(Ph)COPh (1.066 g; 5.00 mmol) in dry benzene (30 ml) was added to $SnCl_4$ (1.303 g; 5.00 mmol) in dry benzene (40 ml) with no visible reaction. After standing for 16 h the volume of the solution was reduced by approximately a half, at which point a white solid formed, and this was filtered off, washed with benzene and dried in vacuo. This was identified as the salt di-*N*-benzoyl-*N*-hydroxy-*N*-phenylammonium hexachlorostannate(IV). Found: C, 41.25; H, 2.91; N, 4.79. $C_{26}H_{24}O_4N_2Cl_6Sn$ calcd.: C, 41.10; H, 3.18; N, 3.69%. Evaporation of the filtrate from the reaction, gave a white residue, which on extraction with chloroform, and subsequent precipitation with methanol gave dichlorotin bis-*N*-benzoyl-*N*-phenylhydroxylamine identified by comparison of its infrared spectrum, with a previously prepared sample.

(m) Dimethylchlorotin N-benzoyl-N-phenylhydroxylamine. Lithium (0.41 g; 5.85 mmol) was dissolved in dry methanol (15 ml) and to this was added HON(Ph)COPh (1.066 g; 5.00 mmol) also in dry methanol (5 ml). $(CH_3)_2SnCl_2$ (1.098 g; 5.00 mmol) in dry methanol (10 ml) was added to previously prepared solution, with the formation of a green colour. On standing a white crystalline

solid formed, which was removed, washed with methanol and ether, and dried in vacuo. Recrystallisation from methanol/chloroform gave dimethylchlorotin *N*-benzoyl-*N*-phenylhydroxylamine (yield: 1.23 g; 62.1%). Found: C, 45.86; H, 3.73; N, 3.34. $C_{15}H_{16}O_2NClSn$ calcd.: C, 45.45; H, 4.07; N, 3.53%. M.p. 160°C. NMR data ($CDCl_3$ soln.): δ 1.06 ppm $(CH_3)_2$, 7.28 (Ph). $^2J(^{119,117}Sn{-}C{-}^2H)$ 79.85, 76.00 Hz.

(n) Dimethylbromotin N-benzoyl-N-phenylhydroxylamine. Lithium (0.037 g; 5.33 mmol), HON(Ph)COPh (1.066 g; 5.00 mmol) and $(CH_3)_2SnBr_2$ (1.543 g; 5.00 mmol) were reacted, and the product extracted and purified as in (m) to give dimethylbromotin-*N*-benzoyl-*N*-phenylhydroxylamine (yield: 1.63 g; 74.3%) as a white crystalline solid (m.p. 174.5°C). Found: C, 40.60; H, 4.12; N, 2.70. $C_{15}H_{16}O_2NBrSn$ calcd.: C, 40.86; H, 3.66; N, 3.18%' NMR data ($CDCl_3$ soln.) δ 1.02 ppm ($(CH_3)_2Sn$), 7.15 (Ph). $^2J(^{119,117}Sn{-}C{-}^1H)$ 76.5 Hz.

(o) Dimethyliodotin N-benzoyl-N-phenylhydroxylamine. Lithium (0.040 g; 5.69 mmol), HON(Ph)COPh (1.066 g; 5.00 mmol) and $(CH_3)_2SnI_2$ (2.013 g; 5.00 mmol) were reacted, and the product extracted and purified as in (m) to give dimethyliodotin *N*-benzoyl-*N*-phenylhydroxylamine (yield: 1.46 g; 59.0%) as a white crystalline solid. Found: C, 36.64; H, 3.81; N, 2.36. $C_{15}H_{16}O_2NISn$ calcd.: C, 36.93; H, 3.31; N, 2.87%. NMR data ($CDCl_3$ soln.) δ 1.35 ppm ($(CH_3)_2Sn$), 7.28 (Ph). $^2J(^{119,117}Sn{-}C{-}^1H)$ 73.4 Hz.

(p) Attempted preparation of triphenyltin N-benzoylhydroxylamine. Ph_3SnOH (3.670 g; 10.00 mmol) and HON(H)COPh (1.411 g; 10.00 mmol) were refluxed together in benzene (55 ml) under Dean and Stark conditions for 14 h. A white solid was formed, which was removed and dried. This was identified as tetraphenyltin, by comparison of its infrared spectrum, with that of a pure sample of Ph_4Sn. Attempts to isolate other products were unsuccessful.

(q) Reaction of triphenyltin chloride, N-benzoylhydroxylamine and triethylamine. Ph_3SnCl (1.927 g; 5.00 mmol) in dry methanol (25 ml) was added dropwise with stirring, to HON(H)COPh (0.686 g; 5.00 mmol) also in dry methanol (25 ml) and anhydrous $(C_2H_5)_3N$ (1.015 g; 10.03 mmol) with no apparent reaction. The mixture was refluxed for six hours, whereupon a solid formed, which was removed and dried, and identified as tetraphenyltin. Found: C, 67.51; H, 5.33; N, 0.00. $C_{24}H_{20}Sn$ calcd.: C, 67.40; H, 4.68; N, 0.00%. The infrared spectrum was also identified as that of tetraphenyltin.

(r) Repeat of (q) with excess triethylamine. Ph_3SnCl (1.927 g; 5.00 mmol), and HON(H)COPh (0.686 g; 5.00 mmol) were mixed as in (q) with a large excess of $(C_2H_5)_3N$, giving the immediate formation of a white solid. The solid was filtered off, washed with methanol and then ether, and dried in vacuo yielding triethylammonium triphenyltin benzohydroximate (yield: 1.10 g; 37.5%) as a white microcrystalline solid. Found: C, 62.26; H, 5.88; N, 3.46. $C_{31}H_{36}O_2N_2Sn$ calcd.: C, 62.25; H, 6.07; N, 4.79%. NMR data ($CDCl_3$ soln.): δ 0.72 ppm (CH_3—) 2.27 (—CH_2—), 7.46, 7.06 (Ph). Mössbauer data IS. 0.59 mm sec^{-1}, QS 1.41 mm sec^{-1}.

(s) Reaction of triphenyltin hydroxide with N-4-methylbenzoylhydroxylamine. Ph_3SnOH (0.824 g; 2.14 mmol) and HON(H)CO · C_6H_4 · CH_3 (0.339 g; 2.24 mmol) were refluxed together in benzene (50 ml) under Dean and Stark conditions, for 6 h, after which no further water separated out. The white precipitate formed was filtered off, and recrystallised from benzene, giving tetra-

phenyltin as a white microcrystalline solid, which was identified from its infrared spectrum. Found: C, 67.63; H, 4.84; N, 0.00. $C_{24}H_{20}Sn$ calcd.: C, 67.49; H, 4.72; N, 0.00%.

(t) Dichlorotin bis-N-benzoylhydroxylamine. $SnCl_4$ (1.620 g; 6.22 mmol) in dry methanol (10 ml) was added dropwise with stirring to potassium benzohydroxamate (2.180 g; 12.44 mmol) in dry methanol (25 ml). A white solid formed on standing, which was removed and recrystallised from a large volume of methanol, to give dichlorotin bis-*N*-benzoylhydroxylamine as a white crystalline solid. Found: C, 36.11; H, 3.23; N, 5.79. $C_{14}H_{12}O_4N_2Sn$ calcd.: C, 36.37; H, 2.59; N, 6.06%.

(u) Dibromotin bis-N-benzoylhydroxylamine. $SnBr_4$ (2.235 g; 5.11 mmol) and potassium benzohydroxamate (1.782 g; 10.16 mmol) were reacted and the solid extracted as described in (t). Found: C, 27.30; H, 2.30; N, 4.54%. $C_{14}H_{12}O_4N_2Br_2Sn$ calcd.: C, 30.53; H, 2.20; N, 5.09%.

(v) Diiodotin bis-N-benzoylhydroxylamine. SnI_4 (1.980 g; 3.16 mmol) and potassium benzohydroxamate (1.369 g; 7.82 mmol) were reacted and the product extracted as described in (t). Recrystallisation of the crude grey product was carried out in chloroform and gave diiodotin bis-*N*-benzoylhydroxylamine as a pale yellow crystalline solid. Found: C, 26.42; H, 2.09; N, 5.22. $C_{14}H_{12}O_4N_2I_2Sn$ calcd.: C, 26.04; H, 1.86; N, 4.34%.

(w) Dimethyltin bis-N-acetyl-N-methylhydroxylamine. $(CH_3)_2SnO$: (1.663 g; 10.10 mmol) and $HON(CH_3)COCH_3$ (0.996 g; 11.18 mmol) were refluxed together in benzene (90 ml) under Dean and Stark conditions for 10 h. On cooling, the excess $(CH_3)_2SnO$ was filtered off, and the filtrate evaporated to dryness, whereupon the solid obtained was recrystallised from chloroform/ether, and dried in vacuo to give dimethyltin bis-*N*-acetyl-*N*-methylhydroxylamine (yield: 0.45; 24.8%) (m.p. 138.5°C) as a white crystalline solid. Found: C, 29.42; H, 5.76; N, 8.39. $C_8H_{18}O_4N_2Sn$ calcd.: C, 29.55; H, 5.58; N, 8.39%. NMR data ($CDCl_3$ soln.): δ 1.83 ppm (CH_3—C), 3.17 ppm (CH_3—N), 0.23 ($(CH_3)_2Sn$), $^2J(^{119,117}Sn—C—^1H)$ 81.5, 77.3 Hz.

(x) Attempted preparation of diphenyltin bis-N-acetyl-N-methylhydroxylamine. Ph_2SnO (1.835 g; 5.00 mmol) and $HON(CH_3)COCH_3$ (0.908 g; 10.19 mmol) were reacted as in (w) to give a cloudy solution on cooling, which after filtration was evaporated to dryness, and the resultant solid recrystallised from chloroform/ether to give a waxy solid. Found: C, 29.41; H, 3.64; N, 5.26. $C_{18}H_{22}O_4N_2Sn$ calcd.: C, 48.2; H, 4.94; N, 6.25%.

(y) Dimethyltin bis-N-acetylhydroxylamine. $(CH_3)_2SnO$ (1.110 g; 6.74 mmol) and $HON(H)COCH_3$ (1.011 g; 13.47 mmol) were reacted as described in (w) and on cooling the white solid was removed and recrystallised from methanol to give dimethyltin bis-*N*-acetylhydroxylamine (yield: 0.64 g; 34.8%) as a white crystalline solid. Found: C, 24.22; H, 4.92; N, 8.89. $C_6H_{14}O_4N_2Sn$ calcd.: C, 24.27; H, 4.72; N, 9.44%. NMR data (CD_3OD soln.): δ 1.12 ppm (CH_3—C), 0.27 ($(CH_3)_2Sn$), $^2J(^{119,117}Sn—C—^1H)$ 77 Hz.

(z) Preparation of dichlorotin bis-N-acetyl-N-methylhydroxylamine. $SnCl_4 \cdot 5\ H_2O$ (1.755 g; 5.00 mmol) and $HON(CH_3)COCH_3$ (1.805 g; 20.26 mmol) were mixed in methanol (30 ml) and refluxed for 5 h. On cooling a white solid precipitated out, which was removed, recrystallised from methanol and dried in vacuo to give dichlorotin bis-*N*-acetyl-*N*-methylhydroxylamine (yield:

0.74 g; 40.4%) as a white crystalline solid. Found: C, 19.66; H, 3.29; N, 7.80%. $C_6H_{12}O_4N_2Cl_2Sn$ calcd.: C, 19.70; H, 3.31; N, 7.77%. NMR data ($CDCl_3$ soln.): δ 2.80 ppm (CH_3—C), 4.11 (CH_3—N).

(aa) Attempted preparation of trimethyltin N-acetyl-N-methylhydroxylamine. $(CH_3)_3SnOH$ (1.348 g; 7.51 mmol) and $HON(CH_3)COCH_3$ (0.668 g; 7.49 mmol) were refluxed together in benzene (50 ml) under Dean and Stark conditions for five hours. On cooling, the almost clear solution was filtered and the filtrate reduced in volume to give a labile oil. Vacuum distillation gave three fractions, which could not be identified. A solid formed slowly in the second fraction (38.5—44.0°C/0.25 mmHg) which also could not be identified.

(bb) Attempted preparation of triphenyltin N-acetyl-N-methyldroxylamine. Ph_3SnOH (1.835 g; 5.00 mmol) and $HON(CH_3)COCH_3$ (0.450 g; 5.05 mmol) were reacted as in (aa). On cooling the insoluble residue was filtered off and the filtrate evaporated to dryness to give an off-white solid, which was recrystallised from chloroform/pentane to give diphenyltin bis-*N*-acetyl-*N*-methylhydroxylamine as a white microcrystalline solid. Found: C, 47.76; H, 4.54; N, 4.78. $C_{18}H_{22}O_4N_2Sn$ calcd.: C, 48.2; H, 4.94; N, 6.25. NMR data ($CDCl_3$ soln.): δ 2.28 ppm (CH_3—C), 3.61 (CH_3—N), 7.76 (*o*-protons Ph), 7.44 (*m*- and *p*-protons Ph).

(cc) Reaction with trimethyltin diethylamine in ether. $(CH_3)_3SnN(C_2H_5)_2$ (1.829 g; 7.75 mmol) in dry ether (8 ml) was added dropwise with stirring to $HON(CH_3)COCH_3$ (0.693 g; 7.78 mmol) in dry ether (40 ml) under argon. After standing for two hours, with no apparent reaction, the solution was refluxed for 30 min and the resulting solution reduced in volume, whereupon large colourless crystals formed. These crystals were removed and recrystallised twice from ether to give dimethyltin bis-*N*-acetyl-*N*-methylhydroxylamine. This was identified from its infrared spectrum and its analysis. Found: C, 29.61; H, 5.93; N, 8.38. $C_8H_{18}O_4N_2Sn$ calcd.: C, 29.47; H, 5.58; N, 8.62%.

(dd) Reaction with trimethyltin diethylamine in n-pentane. $(CH_3)_3SnN(C_2H_5)_2$ (2.240 g; 9.49 mmol) in freshly distilled dry pentane (8 ml) was added dropwise with stirring to a mixture of $HON(CH_3)COCH_3$ (0.806 g; 9.04 mmol) and n-pentane (30 ml) under an argon atmosphere with the immediate formation of a white solid. Filtration gave trimethyltin *N*-acetyl-*N*-methylhydroxylamine (m.p. dec. ca. 70°C) as a white microcrystalline solid. Found: C, 28.35; H, 6.49; N, 5.44. $C_6H_{15}O_2NSn$ calcd.: C, 28.61; H, 6.00; N, 5.56%. NMR data ($CDCl_3$ soln.): δ 3.16 ppm (CH_3—N), 1.86 (CH_3—C), 0.307 ($(CH_3)_3Sn$). $^2J(^{119,117}Sn—C—^1H)$ 54.5, 53.1 Hz.

(ee) Preparation of trimethyltin N-phenyl-N-tosylhydroxylamine. $(CH_3)_3SnOH$ (0.904 g; 5.00 mmol) and $HON(Ph)SO_2C_6H_4 \cdot CH_3$ (1.317 g; 5.00 mmol) were refluxed in benzene (50 ml) under Dean and Stark conditions for 16 h. The cooled solution was filtered and the filtrate evaporated to dryness to give a yellow solid. Extraction of the solid with ethanol and subsequent recrystallisation from ether to give trimethyltin *N*-phenyl-*N*-tosylhydroxylamine as a pale yellow crystalline solid. Found: C, 45.05; H, 5.12; N, 3.03; S, 6.98%. $C_{16}H_{21}O_3NSSn$ calcd.: C, 45.10; H, 4.97; N, 3.29; S, 7.52%. NMR data ($CDCl_3$ soln.): δ 6.95 ppm (Ph), 2.13 (CH_3), 0.28 ($(CH_3)_3Sn$).

(ff) Reaction of N-acetyl-N-methylhydroxylamine with hexamethyldisilazane. Hexamethyldisilazane (2.43 g; 15.06 mmol) in ether (10 ml) was added to HON-

$(CH_3)COCH_3$ (2.700 g; 30.30 mmol) in ether (20 ml) and the resulting solutions refluxed for 4 h, under argon. Reduction of the solution volume gave an oil, which was distilled in vacuo to give three fractions (major fraction collected, 47–48°C/0.005 mmHg). Found: C, 45.82; H, 9.41; N, 17.55. $C_6H_{16}ON_2Si$ ($(CH_3)_3SiNH{-}N(CH_3)COCH_3$) calcd.: C, 44.95; H, 10.06; N, 17.48%. NMR data (C_6H_6 soln.): δ 0.20 ppm ($(CH_3)_3Si$), 2.08 ($CH_3{-}C$), 3.16 ($CH_3{-}N$).

Results and discussion

A. Syntheses

The diorganotin bis-*N*-benzoyl-*N*-phenylhydroxylamine derivatives I were readily prepared in good yields, from the appropriate diorganotin oxide and the hydroxylamine in benzene, by azeotropic removal of water in a Dean and Stark apparatus:

$$R_2SnO + HON(Ph)COPh \rightarrow \underset{(I)}{R_2Sn[ON(Ph)COPh]_2} + H_2O$$

($R = CH_3, C_6H_5$, n-C_4H_9, n-C_8H_{17})

The dimethyl-, diphenyl-, and di-n-butyl-tin derivatives were obtained as very soluble, cream coloured solids and recrystallised with difficulty from hydrocarbonds. The dioctyltin compound was isolated as an undistillable viscous brown oil, which was purified by partition between benzene and aqueous ethanol. Dimethyltin bis-*N*-acetyl-*N*-methylhydroxylamine was obtained similarly, but isolation of the corresponding diphenyltin derivative by the same method proved unsatisfactory.

n-Butyltin tris-*N*-benzoyl-*N*-phenylhydroxylamine (II) was also prepared by azeotropic removal of water, when butylstannonic acid and the hydroxylamine were refluxed together in benzene. However, the similar reaction with phenylstannonic acid and *N*-acetyl-*N*-methylhydroxylamine gave a mixture of products, which proved inseparable.

$$\text{n-}C_4H_9SnO(OH) + 3\ HON(Ph)COPh \rightarrow \underset{(II)}{(\text{n-}C_4H_9)Sn[ON(Ph)COPh]_3} + 2\ H_2O$$

The same procedure was employed for the preparation of trimethyltin *N*-phenyl-*N*-tosyhydroxylamine (III):

$$(CH_3)_3SnOH + HON(Ph)SO_2C_6H_4CH_3 \rightarrow \underset{(III)}{(CH_3)_3SnON(Ph)SO_2C_6H_4CH_3} + H_2O$$

However, attempted syntheses of trimethyltin and triphenyltin *N*-acetyl-*N*-methylhydroxylamine were unsuccessful. In the latter case, diphenyltin bis-*N*-acetyl-*N*-methylhydroxylamine, water, and an insoluble residue were formed, whilst in the former an oil was obtained which decomposed on distillation in vacuo to afford an oil and a solid neither of which were identified.

Addition of *N*-benzoyl-*N*-phenylhydroxylamine to lithium methoxide (prepared in situ by the addition of freshly cut clean lithium metal to dry methanol in an inert atmosphere) in dry methanol under argon, gave pale lemon crystals of lithium *N*-benzoyl-*N*-phenylhydroxylamine, which slowly separated out of solution. The sodium salt of *N*-acetyl-*N*-methylhydroxylamine was prepared in a similar fashion. The lithium salt was used to prepare a series of dihalogenotin bis-*N*-benzoyl-*N*-phenylhydroxylamines (IV) and dimethylhalogenotin *N*-phenylhydroxylamines (V) as white or yellow microcrystalline solids. In each case the lithium salt was prepared in situ, and subsequently reacted with the tin tetrahalides or dimethyltin dihalides respectively, in dry methanol under anerobic conditions.

$$\mathrm{SnX_4 + 2\ LiON(Ph)COPh \rightarrow \underset{(IV)}{X_2Sn[ON(Ph)COPh]_2} + 2\ LiX}$$

$(\mathrm{X = Cl, Br, I})$

$$\mathrm{(CH_3)_2SnX_2 + LiON(Ph)COPh \rightarrow \underset{(V)}{(CH_3)_2Sn(X)[ON(Ph)COPh]} + LiX}$$

$(\mathrm{X = Cl, Br, I})$

The dichlorotin *N*-acetyl-*N*-methylhydroxylamine complex (VI) was obtained by an altogether different route: tin(IV) chloride pentahydrate was refluxed in methanol with *N*-acetyl-*N*-methylhydroxylamine in a molar ratio of 1 : 4, whereupon crystals of the dichlorotin derivative separated out on cooling:

$$\mathrm{SnCl_4 \cdot 5\ H_2O + 4\ HON(CH_3)COCH_3}$$

$$\mathrm{\rightarrow \underset{(VI)}{Cl_2Sn[ON(CH_3)COCH_3]_2} + 2\ HON(CH_3)COCH_3 \cdot HCl}$$

With *N*-benzoyl-*N*-phenylhydroxylamine in a 1 : 2 molar ratio in cold methanol a deep violet colouration was produced immediately, but no product could be isolated.

The mixing of dry benzene solutions of anhydrous tin(IV) chloride and *N*-benzoyl-*N*-phenylhydroxylamine in molar ratio 1 : 1 yielded on reduction of the volume of the solution under reduced pressure, two products, which were separated by recrystallisation from different solvents. The products were identified as the *N*-benzoyl-*N*-phenylhydroxylammonium salt of the hexachlorotin anion VII, and dichlorotin bis-*N*-benzoyl-*N*-phenylhydroxylamine, the excess tin(IV) chloride presumably being taken off in vacuo with the other volatile components of the reaction mixture:

$$\mathrm{4\ Cl_4Sn + 4\ HON(Ph)COPh \rightarrow Cl_2Sn[ON(Ph)COPh_2] + 2\ Cl_4Sn}$$

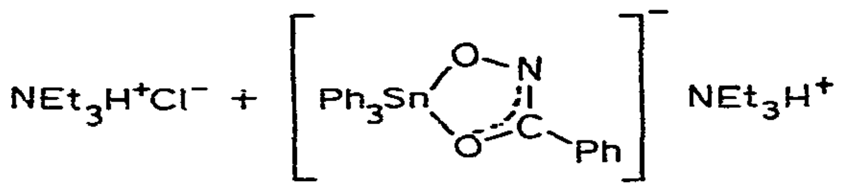
$$\mathrm{+ \underset{(VII)}{[HON(Ph)HCOPh]_2^+[SnCl_6]^{2-}}}$$

The attempted preparation of the tetrakis-*O*-tin-*N*-acetyl-*N*-methylhydroxylamine, from tin(IV) chloride and the sodium salt of the hydroxylamine, was unsatisfactory with no identifiable products being obtained.

The attempted preparation of some triorganotin derivatives was found to yield in many cases the diorganotin bishydroxylamine derivatives. We have previously reported [1] that only tetraphenyltin could be identified from the azeotropic dehydration of a mixture of triphenyltin hydroxide and *N*-benzoylhydroxylamine the expected product, $\mathrm{Ph_3SnON(H)COPh}$, was isolated. A triphenyltin derivative of *N*-benzoylhydroxylamine could be isolated as the triethylammonium salt of the $\mathrm{[Ph_3SnON \cdot C(O)Ph]^-}$ anion (VIII) from the reaction of triphenyltin chloride and the hydroxylamine in excess triethylamine in methanol

[1]:

$$Ph_3SnCl + HON(H)COPh + 2\,NEt_3(excess) \longrightarrow$$



(VIII)

However, when this reaction was repeated with a stoichiometric quantity of triethylamine and refluxed in methanol for 1 h, only tetraphenyltin could again be isolated. Although the other product, $Ph_2Sn[ONHCOPh]_2$, was not isolated in these reactions, diphenyltin bis-*N*-acetyl-*N*-methylhydroxylamine was obtained from the reaction of triphenyltin hydroxide and the hydroxylamine after reflux, and only dimethyltin bis-*N*-acetylhydroxylamine was recovered from the reaction of trimethyltin hydroxide and *N*-acetylhydroxylamine. That the migrating phenyl group arises as a result of the clearage of a tin—carbon (phenyl) bond, rather than from a (1,3) phenyl migration from hydroxylamine to tin, was confirmed by the reaction between *N*-4-methylbenzoylhydroxylamine and triphenyltin hydroxide in boiling benzene which yielded tetraphenyltin and no triphenyl-4-tolyltin.

The cleavage of the tin-bound organic group appears to be facilitated by high reaction temperatures, and the attempted preparation of $(CH_3)_3SnON(CH_3)CO(CH_3)$ (IX) from trimethyltin hydroxide and *N*-methyl-*N*-acetylhydroxylamine in boiling benzene yielded a complex mixture of products. However, this compound was isolated as a white solid by the reaction of the hydroxylamine with trimethylstannyldiethylamine in cold anhydrous ether:

$$(CH_3)_3SnNEt_2 + HON(CH_3)COCH_3 \rightarrow \underset{(IX)}{(CH_3)_3SnON(CH_3)COCH_3} + NEt_2H$$

Reflux of the reaction mixture for 30 min afforded the disproportionation product, $(CH_3)_2Sn[ON(CH_3)COCH_3]$. A dilute chloroform solution of (IX) was found to be stable for several months, and it would appear that the disproportionation reaction is thermally-activated. Indeed treating a solid sample of (IX) to ca. 70°C resulted in complete disproportionation:

$$2(CH_3)_3SnO(CH_3)COCH_3 \rightarrow (CH_3)_2Sn[ON(CH_3)COCH_3]_2 + (CH_3)_4Sn$$

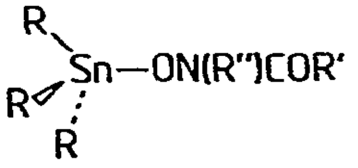
Rather surprisingly, the reaction of *N*-acetyl-*N*-methylhydroxylamine with hexamethyldisilazane did not yield the *O*-silylhydroxylamine. Instead N—O bond fission occurred yielding the *N*-trimethylsilylhydrazine derivative (XI):

$$(CH_3)_3SiNHSi(CH_3)_3 + HON(CH_3)COCH_3 \begin{array}{l} \not\nearrow (CH_3)_3SiON(CH_3)COCH_3 \\ \searrow (CH_3)_3SiNH{-}N(CH_3)COCH_3 \end{array}$$

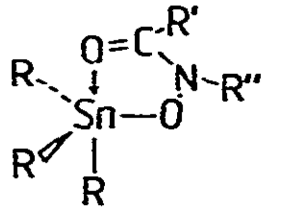
(XI)

B. Spectroscopy-structure correlations

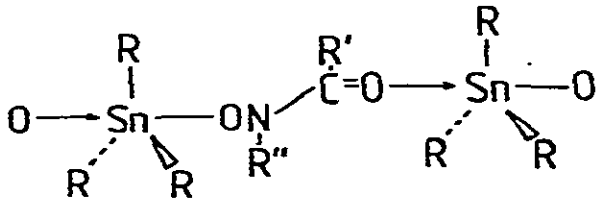
(i). O-Triorganotinhydroxylamines. The presence of a second donor site in the *N*-acylhydroxylamine ligand permits its potential function as a unidentate, or a chelating or bridging bidentate ligand, thus giving rise to the possible four-coordinated structure (XII) or the two five-coordinated structures XIII and XIV, respectively.



(XII)



(XIII)



(XIV)

We have previously shown that both trimethyltin [6] and triphenyltin *N*-benzoyl-*N*-phenylhydroxylamine [2] possess structure XIII in the crystal. The covalent tin—oxygen bond formed by the nitrogen bonded atom is in each case substantially shorter (mean 2.100(6) Å) than the coordinate bond of the axial site (mean 2.318(6) Å). Similarly, whilst the tin—carbon bonds of the equatorial positions are approximately equal in length (2.11(1) Å, 2.14(1) Å), that of the remaining axial site is longer (2.22(1) Å, 2.18(1) Å).

The coordination of the carbonyl group is indicated in the infrared spectrum of these compounds by a substantial reduction in the carbonyl stretching frequency (1540 cm^{-1}) in comparison with the parent hydroxylamine (1620 cm^{-1}), which is itself subject to substantial intramolecular hydrogen-bonding, and so is lower than might be expected. The value observed for trimethylsilyl-*N*-benzoyl-*N*-phenylhydroxylamine (1660 cm^{-1}) is probably more realistic for a "free" carbonyl group in this type of compound [1].

In contrast, trimethyltin *N*-acetyl-*N*-methylhydroxylamine exhibits quite different spectroscopic properties. The Mössbauer QS value for solid $(CH_3)_3SnON(CH_3)COCH_3$ (Table 1) is significantly larger (3.35 mm sec^{-1}) than for the triphenyltin and trimethyltin derivatives of the *N*-benzoyl-*N*-phenylhydroxylamine ligand (1.94 and 2.36 mm sec^{-1}, respectively), indicate of a gross structural change at tin. The QS value falls within the range attributed to trialkyltin compounds with structure XIV by Bancroft et al. [12] and consequently is very similar to that of trimethyltin acetate (IS 1.34 mm sec^{-1}, QS = 3.47 mm sec^{-1}) [13] which is known to have this structure, with the planar trimethyltin moieties bridged by the carboxylate residues [14]. Tetrahedral coordination about the tin in $(CH_3)_3Sn[ON(CH_3)COCH_3]$ may be excluded, since the QS values of less than 2 mm sec^{-1} would be expected for this geometry.

The PMR spectrum of $(CH_3)_3Sn[ON(CH_3)COCH_3]$ in $CDCl_3$ exhibits the

TABLE 1

THE MOSSBAUER SPECTRA OF THE ORGANO- AND HALOGENO-TIN(IV) HYDROXYLAMINES [a]

Compound	IS [b,c]	QS [b,c]	Γ_1 [b]	Γ_2 [b]
$(CH_3)_3Sn[ON(C_2H_5)_2]$ [d]	1.40	1.98	1.26	1.22
$(CH_3)_3Sn[ON(Ph)COPh]$ [d]	1.34	2.36	1.39	1.36
$(CH_3)_3Sn[ON(H)COPh]$ [d]	1.37	2.74	1.55	1.55
$(CH_3)_3Sn[ON(Ph)SO_2C_6H_4 \cdot CH_3]$	1.34	2.66	0.78	0.72
$(CH_3)_3Sn[ON(CH_3)COCH_3]$	1.23	3.36	0.80	0.93
$Ph_3Sn[ON(Ph)COPh]$ [d]	1.26	1.94	0.92	0.92
$(CH_3)_2Sn[ON(Ph)COPh]_2$	1.16	3.07	0.95	0.95
$(CH_3)_2Sn[ON(CH_3)COCH_3]_2$	1.19	3.31	1.01	0.99
$(CH_3)_2Sn[ON(H)COCH_3]_2$	0.93	2.01	0.85	0.90
$(n\text{-}C_4H_9)_2Sn[ON(Ph)COPh]_2$	1.34	3.30	2.76	2.50
$(n\text{-}C_8H_{17})_2Sn[ON(Ph)COPh]_2$	1.23	2.91	0.83	1.45
$Ph_2Sn[ON(Ph)COPh]_2$	0.83	1.80	1.89	2.12
$Ph_2Sn[ON(CH_3)COCH_3]_2$	1.17	1.61	0.97	0.94
$n\text{-}C_4H_9Sn[ON(Ph)COPh]_3$	0.76	2.05	0.75	0.79
$Cl_2Sn[ON(Ph)COPh]_2$	0.41	0	2.37	—
$Br_2Sn[ON(Ph)COPh]_2$	0.50	0	1.39	—
$I_2Sn[ON(Ph)COPh]_2$	0.69	0	1.36	—
$Cl_2Sn[ON(CH_3)COCH_3]_2$	0.35	0	1.08	—
$(CH_3)_2Sn(Cl)[ON(Ph)COPh]$	1.18	2.71	1.29	1.30
$(CH_3)_2Sn(Br)[ON(Ph)COPh]$	1.19	2.65	0.77	0.80
$(CH_3)_2Sn(I)[ON(Ph)COPh]$	1.24	2.63	1.07	1.08

[a] Recorded at 77 K. [b] mm sec^{-1}. [c] Estimated errors: ±0.05 mm sec^{-1} (IS), ±0.10 mm sec^{-1} (QS). [d] Data taken from ref.

expected proton signals resulting from the three dissimilar methyl groups, in the correct integrated ratios. However, the value of the coupling constant $^2J(^{119}Sn—C—^1H)$ is 54.5 Hz, similar to that observed for $(CH_3)_3Sn[ON(Ph)COPh]$ (Table 2) which was assigned a *cis*-trigonal bipyramidal structure XIII in solution [1]. The *trans*-trigonal bipyramidal $(CH_3)_3SnX_2$ species are expected to have $^2J(^{119}Sn—C—^1H)$ values of ca. 70 Hz commensurate with an approximately sp^2 rehybridisation for the planar $(CH_3)_3Sn$ group. The value of the coupling constant, here, is related to the *s*-electron density directed along the tin—carbon bond, via the Fermi contact mechanism, a value of 70 Hz indicates a high degree of *s*-electron density (ca. 33%), whilst a value of 50 Hz is expected for four-coordinate sp^3 hybridised species, such as $(CH_3)_3Sn$, and indicates a lower degree of *s*-electron character (ca. 25%). Although a tetrahedral four-coordinate structure for $(CH_3)_3Sn[ON(CH_3)COCH_3]$ in solution cannot be ruled out on the basis of PMR data alone, the low coupling constant values of this compound, and $(CH_3)_3Sn[ON(Ph)COPh]$, can be rationalised in terms of a *cis*-R_3SnX_2 trigonal bipyramidal structure XIII by considering the pyramidal $(CH_3)_3Sn$ group as the base of a distorted tetrahedral R_3SnX species, with small C—Sn—C bound angles. In addition, rehybridisation can be expected to lead to reallocation of the available *s*-electron density into the bonds to carbon, away from the electronegative oxygen atoms of the ligand, as predicted by Bent [15].

The bidentate nature of the ligand in $(CH_3)_3Sn[ON(CH_3)COCH_3]$ is immediately obvious in both the solid and solution (5% in CH_2Cl_2) infrared spectra (Ta-

TABLE 2

^{119,117}Sn—C—^{1}H COUPLING CONSTANTS AND TIN—METHYL PMR CHEMICAL SHIFTS FOR THE METHYLTIN HYDROXYLAMINES

Compound	Solvent	$^2J(^{119}$Sn—C—^{1}H)^a	$^2J(^{117}$Sn—C—^{1}H)^a	$^2J(^{119,117}$Sn—C—^{1}H)^a	δ(Me—Sn)
$(CH_3)_3Sn[ON(Ph)SO_2C_6H_4 \cdot CH_3]$	$CDCl_3$			56.0	0.28
$(CH_3)_3Sn[ON(CH_3)COCH_3]$	$CDCl_3$	54.5	53.1		0.31
$(CH_3)_3Sn[ON(Ph)COPh]$ ^{b}	$CDCl_3$	55.9	54.4		0.46
$(CH_3)_3Sn[ON(H)COPh]$ ^{b}	CH_2Cl_2	56.7	54.3		0.38
$(CH_3)_2Sn[ON(CH_3)COCH_3]_2$	$CDCl_3$	81.5	77.3		0.23
$(CH_3)_2Sn[ON(Ph)COPh]_2$	$CDCl_3$	78.7	75.0		0.78
$(CH_3)_2Sn[ON(H)COCH_3]_2$	CD_3OD			77.0	−0.27
$(CH_3)_2Sn(Cl)[ON(Ph)COPh]$	$CDCl_3$	79.9	76.0		1.06
$(CH_3)_2Sn(Br)[ON(Ph)COPh]$	$CDCl_3$			76.5	1.02
$(CH_3)_2Sn(I)[ON(Ph)COPh]$	$CDCl_3$			73.4	1.35

^{a} Hz. ^{b} Data taken from ref. 1.

ble 3) from the lowering of the carbonyl stretching frequency, which in the free hydroxylamine, $HON(CH_3)COCH_3$, is considerably higher (1621 cm^{-1}), and like HON(Ph)COPh discussed above can be expected itself to be lower, as a result of internal hydrogen bonding, than the norm for a free carbonyl. The carbonyl stretching frequency of the solid (1589 cm^{-1}) is also significantly lower than that of the solution (1605 cm^{-1}) suggesting stronger coordination of the acyl oxygen to the tin in the solid.

TABLE 3

SOLID AND SOLUTION INFRARED SPECTRA OF $(CH_3)_3Sn[ON(CH_3)COCH_3]$

IR (solid) [a]	IR (soln.) [b]	Assignment
3035vw(sh)	3046w	ν_a(C—H)Sn
2999m	2980mw	ν_a(C—H)
2927m	2939w(sh)	ν_a(C—H)Sn
	2917w	
2876mw		ν_s(C—H)
	2023vw	
	1929vw(br)	
1737vvw		
1699vvw		
1589vvs	1605vvs	ν(C=O)
1494vs	1486mw	
1443s		
1418vs	1419mw(sh)	ν(C—N)
	1410mw	
1388vs	1386w(sh)	δ_a(C—H)Sn
	1376w	
1356s	1365w	
	1308w	
	1274w	
	1250vw(sh)	
1199s	1192vw(sh)	δ_a(C—H)Sn
1189ms(sh)	1160mw	
1144vvw		
1031vvw	1028vw	
	968m	
948mw		ν(N—O)
	926vvw(br)	
	902vvw(br)	
	887vvw(br)	
804w(sh)		
774ms(br)	770vw(br)	r(CH_3—Sn)
762ms		
	680vw	
667w(br)		
617vvw	623mw	
	598vw	
580vvw	553w(sh)	ν(Sn—O)
550m		ν_s(Sn—C)
	541m	
	519w	ν(Sn—C)
	506w	
502vw		ν(Sn———O)
	482vw	ν(Sn———O)
434w		
362vvw(br)		
322vw(br)		

[a] Halocarbon and nujol mulls. [b] 5% solution in CH_2Cl_2.

The difference in structure of $(CH_3)_3Sn[ON(CH_3)COCH_3]$ in solution from that in the solid state, as indicated by the Mössbauer and PMR spectra, in the reflected by the difference in the infrared spectra (Table 3), particularly in the region 600—250 cm^{-1} which normally contains the tin—carbon and tin—oxygen stretching modes. Group-theoretical predictions for a *trans*-MX_3Y_2 trigonal bipyramidal species (point group D_{3h}) suggest a Raman active A_1(M—X) mode and a Raman and infrared active E(M—X) mode, whereas for the *cis*-MX_3Y_2 trigonal bipyramidal species (point group C_{2v}) the B_2 and $2A$(M—X) modes are all infrared active. The solid spectrum of $(CH_3)_3Sn[ON(CH_3)COCH_3]$ has three bands within the tin—carbon stretching region, very weak at 580 and 502 cm^{-1} and a medium intense band at 550 cm^{-1}. The more intense band is immediately assigned the tin—carbon stretching mode, and the weak band at 580 cm^{-1} can be disregarded as a Sn—C mode, since it is too high to be a symmetric mode and too weak to be an antisymmetric mode, however the band at 502 cm^{-1} could be associated with a Sn—C mode. The spectrum is best rationalised in terms of the *trans*-MX_3Y_2 structure XIV, with the band at 550 cm^{-1} assigned to a tin—oxygen mode, or to the A_1 mode, which is rendered infrared active by distortion of the planar MX_3 group. However, the solution spectrum, shows five bands in the tin—carbon stretching region, one of which (598 cm^{-1}) is higher than those normally associated with methyltin compounds, and the remaining four medium and weak bands (553, 541, 519 and 506 cm^{-1}), three of which can be assigned to tin—carbon stretching modes suggest the *cis*-MX_3Y_2 structure XIII, containing the pyramidal $(CH)_3Sn$ group, predicted on the basis of the PMR spectrum.

The major fragments of the mass spectrum $(CH_3)_3Sn[ON(CH_3)COCH_3]$ (Table 4), indicate no ditin containing fragments and shows the monomer parent

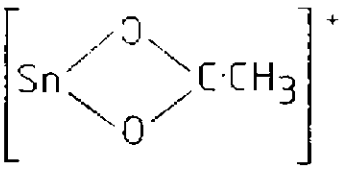
TABLE 4

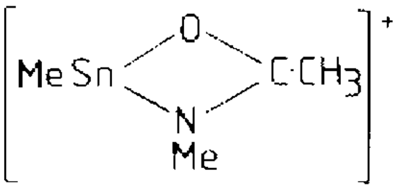
THE MAJOR FRAGMENTS IN THE MASS SPECTRUM OF $(CH_3)_3Sn[ON(CH_3)COCH_3]$ [a,b]

m/e	Relative intensity [c]	Assignment
252	1.08	$(CH_3)_3Sn[ON(CH_3)COCH_3]^+$
237	100.00	$(CH_3)_2Sn[ON(CH_3)COCH_3]^+$
228	16.15	
221	5.38	$(CH_3)_2SnN(CH_3)COCH_3^+$
207	64.62	$Sn[ON(CH_3)COCH_3]^+$
184	57.69	
178	10.15	$SnO_2CCH_3^+$
164	9.62	$(CH_3)_3Sn^+$
154	19.23	
149	23.08	$(CH_3)_2Sn^+$
136	7.69	$SnOH^+$
134	23.85	$(CH_3)Sn^+$
120	10.77	SnH^+
119	23.08	Sn^+
100	9.23	
89	13.46	$HON(CH_3)COCH_3^+$
73	59.23	$ON{=}COCH_3^+$
58	10.62	$ON{=}CO^+$
56	10.12	
43	1.62	$COCH_3^+$

[a] Mass count based on ^{119}Sn. [b] Direct insertion at 60°C. [c] Based on the most intense tin containing fragment.

ion as the highest mass ion at m/e 252, contrary to expectation, since the Mössbauer and solid state infrared suggest an associated structure. This is perhaps to be expected since the compound melts with decomposition at ca. 70°C and it is not unreasonable to expect the compound, which rearranges readily on solution to the monomer, to adopt the monomeric structure in the gas phase. The base ion occurs at m/e 237, and corresponds to the loss of one methyl group from parent: it is significant that the loss of a second methyl group does not appear as favourable. One fragment, m/e 178, appears to correspond to an ion XV arising from the ring contraction of the chelate ring by the loss of the nitrene species [CH_3N:], and the fragment m/e 221 corresponds to an ion XVI, which presumably arises as the result of a ring contraction by loss of an oxygen atom from the chelate ring. Such ring-contraction processes have also been observed in the mass spectra of the triorganotin *N*-benzoyl-*N*-phenylhydroxylamine derivatives [1]. The remaining fragments result primarily from the straightforward stripping of substituents from the parent, however three tin-containing fragments remain unassigned (*m/e* 228, 184 and 154), and presumably arise as the result of complex rearrangement products, formed during the compound heat-up.

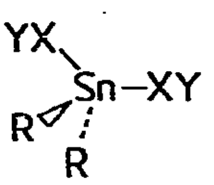

(XV)


(XVI)

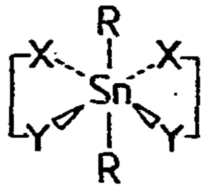
Trimethyltin-*N*-phenyl-*N*-tosylhydroxylamine has a QS value (2.66 mm sec^{-1}), which is just outside the range defined by Bancroft and coworkers [12] for compounds having *cis*-R_3SnL_2 structures, however the value is within those found for the other triorganotin hydroxylamines (Table 1), which we have assigned the *cis* structure XIII. The compound is not tetrahedral, since for such a structure a QS value of <2 mm sec^{-1} would be expected and so presumably involves a bidentate hydroxylamine group, the coordinate bond to tin being formed by one of the sulphonyl oxygens. It is conceivable that the other oxygen atom of the sulphonyl group also coordinates to form a six-coordinate geometry at tin, but this is unlikely. In solution, the compound has a PMR coupling constant $^2J(^{119,117}Sn—C—^1H)$, similar to those observed for both $(CH_3)_3Sn[ON(CH_3)COCH_3]$ and $(CH_3)_3Sn[ON(Ph)COPh]$ (Table 2), which were rationalised in terms of pyramidal $Sn(CH_3)_3$ moieties. The evidence suggests that $(CH_3)_3Sn[ON(Ph) \cdot SO_2 \cdot C_6H_4CH_3]$ like $(CH_3)_3Sn[ON(Ph)COPh]$ has a *cis*-R_3SnL_2 trigonal bipyramidal structure XIII in both solution and solid phases.

(ii) O,O'-Diorganotin bishydroxylamines. The diorganotin derivatives, $R_2Sn[X—Y]_2$, of the potentially bidentate ligand, X—Y, may assume any one of several possible stereochemistries. When the chelating ligand has a weak second donor site, then tetrahedral compounds XVII can be expected, particularly when the R groups sterically crowd the first-coordination sphere of the tin. When the second donor site of the ligand is more strongly coordinating, then octahedral configurations about the tin are formed, and if the chelate bonds intramolecularly to form discrete molecular species, two stereochemistries can be formed, *trans*-$R_2Sn(X—Y)_2$ XVIII, and *cis*-$R_2Sn(X—Y)_2$ XIX. It is clear that

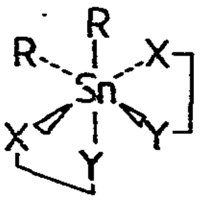
the relative arrangement of the chelating ligand, X—Y, can also lead to other



(XVII)

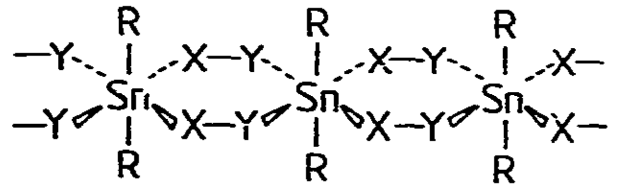


(XVIII)

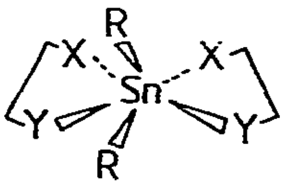


(XIX)

choices of stereochemistry, however selection of the relative orientation of the chelate is difficult, in the absence of crystallographic evidence, particularly, as in the case of the *N*-acylated hydroxylamines, the donor atoms are of the same type. Intermolecular coordination of the chelate, leads to the formation of dimeric, or polymeric structures, where R_2Sn moieties are bridged by the chelate XX, and again several isomeric types are conceivable.



(XX)

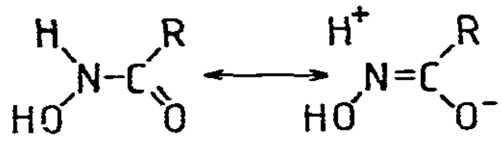


(XXI)

The Mössbauer parameters of the seven diorganotin derivatives of hydroxylamines investigated, exhibit two ranges of QS values (Table 1). The QS of dimethyltin bis-*N*-acetyl-*N*-methylhydroxylamine, $(CH_3)_2Sn[ON(CH_3)COCH_3]_2$, which is known to have the *trans*-$R_2Sn(X—Y)_2$ distorted octahedral structure XXI, with a carbon—tin—carbon bond angle of 145.8° [3], is similar (3.31 mm sec^{-1}) to those exhibited by the dialkyltin derivatives of the *N*-benzoyl-*N*-phenylhydroxylamine ligand, $(CH_3)_2Sn[ON(Ph)COPh]_2$ (3.07 mm sec^{-1}), $(n\text{-}C_4H_9)_2Sn[ON(Ph)COPh]_2$ (3.30 mm sec^{-1}), and $(n\text{-}C_8H_{17})_2Sn[ON(Ph)COPh]_2$ (2.91 mm sec^{-1}. Although the substituents of the hydroxylamine residue can be expected to effect the coordination of the group, the effect can be considred minimal, and it is reasonable to assume that the structures of these dialkyl species are similar. This suggests that, like $(CH_3)_2Sn[ON(CH_3)COCH_3]_2$, they all have the distorted *trans*-$R_2Sn(XY)_2$ structure XXI.

The diphenyltin derivatives of the hydroxylamines, $HON(CH_3)COCH_3$, and HON(Ph)COPh have substantially lower QS, values (1.61 and 1.80 mm sec^{-1}, respectively) than the previously mentioned dialkyltin derivatives. Dimethyltin bis-*N*-acetylhydroxylamine, however has a low QS (2.01 mm sec^{-1}). Although it is conceivable that these low QS values are commensurate with tetrahedral structures for these compounds, the infrared data (see below) makes this unlikely, and the values suggest *cis*-$R_2Sn(X—Y)_2$ octahedral structures XIX. By assuming idealised octahedral structures for $(CH_3)_2Sn[ON(CH_3)COCH_3]_2$ and $(CH_3)_2Sn\text{-}ON(Ph)COPh]_2$, and that the covalent and coordinate oxygen atoms are equivalent in respect of the tin, the partial quadropole splitting (PQS) values of the two ligands can be evaluated (PQS $\frac{1}{2}[ON(CH_3)COCH_3] = -0.203$ mm sec^{-1}; and PQS $\frac{1}{2}[ON(Ph)COPh] = -0.214$ mm sec^{-1}) by application of a point charge calculation. Application of these values to the diphenyl cases predicts for: *cis*-$Ph_2Sn[ON(CH_3)COCH_3]_2$, QS 1.50 mm sec^{-1}; *trans*-$Ph_2Sn[ON(CH_3)COCH_3]_2$, QS 2.99 mm sec^{-1}; and *cis*-$Ph_2Sn[ON(Ph)COPh]_2$, QS 1.46 mm sec^{-1}; *trans*-$Ph_2Sn[ON(Ph)COPh]_2$, QS —2.95 mm sec^{-1}. Although it was not possible to determine the sign of the

QS in the present case, the values of the calculated QS indicate that the *cis*-$R_2Sn(X{-}Y)_2$ geometry is more likely for both diphenyl derivatives, and reasonable agreement between the calculated and observed QS values was found, in spite of the rather gross assumptions employed. Utilising a PQS value of -0.203 mm sec^{-1} for $\frac{1}{2}[ON(H)COCH_3]$, point charge calculations predict for *cis*-$(CH_3)_2Sn[ON(H)COCH_3]_2$, QS 1.56 mm sec^{-1} and for *trans*-$(CH_3)_2Sn[ON(H)COCH_3]_2$, QS 3.31 mm sec^{-1}. The hydroxamic acids exhibit tautomeric behaviour XXII.



(XXII)

and thus we might expect the acyl oxygen to coordinate more strongly with the tin atom, on coordination. Such action increases the covalency of the coordinate bond, and decreases the PQS value for the ligand, which in turn increases the QS for both *cis* and *trans* configurations, suggesting the *cis* configuration for this compound. The tautomerism of the nitrogen substituted hydroxamates, $HON(CH_3(COCH_3$, and HON(Ph)COPh, is limited by the electron donating ability of the nitrogen substituents. Although the value of the QS of *cis*-octahedral diorganotin compounds has been shown to be dependent on small distortions in the carbon—tin—carbon bond angle [16], the value in this case clearly indicates a *cis* structure.

The PMR spectra of the diorganotin bishydroxylamine derivatives all exhibit the expected proton signals in the correct integrated ratios, and dimethyltin compounds, $(CH_3)_2Sn[ON(CH_3)COCH_3]_2$, $(CH_3)_2Sn[ON(Ph)COPh]_2$ and $(CH_3)_2Sn[ON(H)COCH_3]_2$ showed the usual tin—proton coupling associated with tin—methyl compounds (Table 2). The value of $^2J(^{119}Sn{-}C{-}^1H)$ for $(CH_3)_2Sn[ON(CH_3)COH_3]_2$ was found to be 81.5 Hz. The corresponding coupling constant for *cis*-octahedral $(CH_3)_2Sn[oxin]_2$, which has a carbon—tin bond angle of 110.7° [17] is 71.2 Hz [18] and 99.3 Hz for $(CH_3)_2Sn[acac]_2$ [19] with a linear carbon—tin—carbon moiety [20]. The carbon—tin—carbon bond angle of $(CH_3)_2Sn[ON(CH_3)COCH_3]_2$ is 145.8° [3], and thus the observed coupling constant in solution is in keeping with the retention of the solid-state structure on dissolution, intermediate between carbon—tin—carbon angles of 110.7° and 180°. The $^2J(^{119}Sn{-}C{-}^1H)$ values for $(CH_3)_2Sn[ON(Ph)COPh]_2$ and $(CH_3)_2Sn[ON(H)COCH_3]_2$ (78.7 and 77.0 Hz, respectively) are similar, again suggesting distortion of the CSnC moiety, although not to the same extent as observed for *cis*-octahedral $(CH_3)_2Sn[oxin]_2$. The *cis* structure suggested for $(CH_3)_2Sn[ON(H)COCH_3]_2$ in the solid-state from the Mössbauer data (Table 1) has been confirmed by X-ray crystallography [4]. Thus, it would appear that a structural change occurs upon dissolution involving a change in stereochemistry at tin from *cis*- to distorted *trans*-octahedral, similar to that observed upon the formation of the monodrate in the crystal [4].

The infrared carbonyl stretching frequencies of the diorganotin bis-hydroxylamines ($R_2Sn[ON(Ph)COPh]_2$; R = CH_3, 1560, 1546 cm^{-1}; R = n-C_4H_9, 1564, 1522 cm^{-1}; R = n-C_8H_{17}, 1547 cm^{-1} and $(CH_3)_2Sn[ON(CH_3)COCH_3]_2$, 1609 cm^{-1}) (Tables 5—8) are considerably reduced in comparison to the free hydroxylamines, (HON(Ph)COPh, 1622 cm^{-1} and HON(CH_3)$COCH_3$, 1621 cm^{-1}) again confirming the bidentate nature of the hydroxylamine groups. This situation is not, however, the case with the *N*-acetyl-hydroxylamine and its dimethyltin-bis-derivative, which have similar carbonyl stretching frequencies (HON(H)$COCH_3$, 1605 cm^{-1} and $(CH_3)_2Sn[ON(H)COCH_3]_2$, 1608 cm^{-1} (Table 9). This would appear to result from considerable contribution to the hydroxamic configuration XXII, effectively increasing the carbon—nitrogen bond order and reducing the carbon—oxygen bond order. The free ligand is also capable of considerable inter- and intra-molecular hydrogen bonding, in both its tautomeric forms.

Both the Raman and infrared spectra of $(CH_3)_2Sn[ON(CH_3)COCH_3]_2$ in the solid state have been measured (Table 8) and partially assigned. Group theoretical treatment for an idealised *trans*-$R_2Sn[O]_4$ octahedral species (D_{4h}) predicts two tin—carbon normal stretching modes ($A_{1g} + A_{2u}$), one of which will be solely Raman active (the symmetric stretching mode, ν_s(Sn—C)), and one solely infrared active (the antisymmetric stretching mode, ν_a(Sn—C)). Since the environment about the tin is known to be distorted from the idealised structure, selection rules can be expected to breakdown. The symmetric mode is clearly evident as an intense band at 515 cm^{-1} in the Raman and as a weak band in the infrared at 518 cm^{-1}. Selection of the antisymmetric mode is confined to the two bands in the infrared, at 571 and 550 cm^{-1}, both of which are mirrored in the Raman by weaker bands. The stronger band at 571 cm^{-1}, is assigned to the antisymmetric mode, whilst the other band is probably a tin—oxygen stretching mode.

The infrared spectrum of $(CH_3)_2Sn[ON(Ph)COPh]_2$, (Table 5) contains four absorptions in the 500—600 cm^{-1}, which are mirrored in the Raman, however, the symmetric tin—carbon stretching mode is again obvious at 517 cm^{-1} as a band of medium intensity in the Raman and a weak band in the infrared. The antisymmetric tin—carbon stretching mode is again not obvious, but, again probably is best assigned to the most intense band in this region, at 566 cm^{-1} in the infrared, which also appears inthe Raman as a very weak band.

The vibrational spectra of $(n\text{-}C_4H_9)_2Sn[ON(Ph)COPh]_2$ (Table 6) are subject to the above selection rules for the tin—carbon stretching modes, however the interpretation of the spectra of n-butyltin derivatives is occasionally complicated by the presence of *trans*- and *gauche*-rotamers of the n-butyl group [21]. The appearance of one symmetric tin—carbon stretching band at 610 cm^{-1} in the infrared only, are in keeping with previous assignments for six-coordinate di-n-butyltin complexes [21]. However, as can be seen by comparison with the spectra of $(CH_3)_2Sn[ON(Ph)COPh]_2$, the antisymmetric mode coincides with a very weak ligand vibration, although the increased intensity of this absorption is commensurate with the assignment. The appearance of single symmetric and antisymmetric tin—carbon stretching modes suggests that n-butyl groups adopt the *trans*-rotamer configuration only. This conclusion is physically reasonable since the compact *trans*-rotamer would be more compatible with a sterically crowded six-coordinate tin atom. The mutual exclusion of the infrared and Raman spectra in the tin—carbon stretching region suggests a linear C—Sn—C moiety and a *trans*-$R_2Sn[O]_4$ octahedral structure.

The vibrational spectra of $(CH_3)_2Sn[ON(H)COCH_3]_2$, in the solid-state (Table 9) exhibit three bands in the tin—carbon stretching region. The application of

(Continued on p. 32)

TABLE 5

VIBRATIONAL SPECTRA OF $(CH_3)_2Sn[ON(Ph)COPh]_2$

IR [a]	Raman [b]	Assignment
3076vw	3072vw	ν(C—H)z_1
3057vw		ν(C—H)z_3
3014vvw(br)		ν_a(C—H)
	3002vvw(sh)	
2920vvw	2916vvw	ν_s(C—H)
2348vvw(br)	2060vw	Combinations
1974vvw		
1961vvw(br)		
1939vvw(br)		
1887vvw(br)		
1867vvw(br)		
1837vvw(br)		
1788vvw(br)		
1733vvw(br)		
1715vvw(br)		
1601mw	1601vs	ν(C—C)k
1589s	1588mw(sh)	ν(C—C)e
1560vvs	1560vvw	ν(C=O)
1546vvs	1548vvw	
	1501s	ν(C—C)m
1493s		
1458mw	1462m	ν(C—C)n
1446s	1449w	ν(C=N)
1440m(sh)	1444w(sh)	
1422m	1422vvs	δ_a(C—H)Sn
1319vw		ν(C—C)o
1306vw	1309vvw	β(C—H)e
1291vvw		β(C—H)e
1281vvw	1283s	X-sens. q
	1200vw	δ_s(C—H)Sn
1185vvw	1180w	β(C—H)a
1160mw	1163mw	β(C—H)a
1151vw(sh)		
1101vvw(br)		
1076w	1080vvw	β(C—H)d
1037m	1037vvw	
1016s	1021vvw	β(C—H)b
1002w	1002vs	Ring p
983vw	989vvw	γ(C—H)j
938ms		
936ms		ν(N—O)
926s		
904w		γ(C—N)i
852vvw	858vvw	
832vw	831vvw	γ(C—H)g
797w(sh)		
779ms		X-sens. r
764vvs	768vvw	
731w(sh)	729vvw	γ(C—H)f
725mw	718vvw	
705vs	709vvw	
690vs	690vvw	ϕ(C—C)v
666ms	668vvw	
617vw(sh)	619w	α(C—C—C)s
609w	609vw	
601vw	600vvw	
566mw	566vvw	ν_a(Sn—C)
552vw	556vvw	

TABLE 5 (Continued)

IR [a]	Raman [b]	Assignment
536w	535vvw	ν_a(Sn—O)
517vw	517m	ν_s(Sn—C)
	503vvw	
496ms		ν_a(Sn—O)
	474vvw	
	463vvw	
430mw	430vvw	
423mw		
	409w	ϕ(C—C)w
382vvw(br)		
369vvw(br)	372vvw	
353vw	293vvw	X-sens. t
	228vvw	X-sens. x
	198vw	
	167vvw	

[a] Recorded as nujol and halocarbon mulls. [b] Compacted powder.

TABLE 6

VIBRATIONAL SPECTRA OF $(n\text{-}C_4H_9)_2Sn[ON(Ph)COPh]_2$

IR [a]	Raman [b]	Assignment
3070ms	3065vw	ν(C—H)z_1
2962vs		
2928vs		
2880ms		
2862s		
1967vvw(br)		Combinations
1930vvw(br)		
1826vvw(br)		
1601m	1602vs	ν(C—C)k
1586vvs		ν(C—C)l
1564vvs		ν(C=O)
1552vvs		
1497s(sh)	1497mw	ν(C—C)m
1493s		
1459s	1459s	ν(C—C)n
1447vs		
1422s	1423m	δ_a(C—H)
1378m		
1342w		
1317vw		ν(C—C)o
1308vw		β(C—H)e
1296vw		δ_s(C—H)
1291vw	1285w	δ_s(C—H)
1278vw	1276mw	X-sens. q
1192vvw(sh)		
1183vw(sh)		
1172w(sh)		β(C—H)a
1162ms		
1156m(sh)	1157mw	β(C—H)c
1078m		β(C—H)d
1038ms		
1017vs	1018vvw	β(C—H)b
1004w	1001vvs	Ring p
978vvw		γ(C—H)j

TABLE 6 (Continued)

IR [a]	Raman [b]	Assignment
964vvw		γ(C—H)h
937s		
928vs		ν(N—O)
922ms(sh)		
913s		
882vw		γ(C—H)i
874vw(sh)	875vvw	
868vw(sh)		
852vvw(br)		
839vw		γ(C—H)g
829vvw		
806vvw		
783vs	785vw	
774s		X-sens. r
767vs		
723s	725vw	γ(C—H)f
706vvs	708vvw	
696vs		
692vs		φ(C—C)v
668s		
619w	615mw	α(C—C—C)s
610mw		ν_a(Sn—C)
600vw(sh)		
	592m	ν_s(Sn—C)
550w		ν_a(Sn—O)
538mw	541vw	
498s	493w	ν_a(Sn—O)
432s		
	404vvw	φ(C—C)w
370vw		
352vw		
295vvw(br)	247w	

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[a] Recorded as nujol and halocarbon mulls. [b] Compacted powder.

TABLE 7

THE INFRARED SPECTRA OF SOME ORGANOTIN DERIVATIVES OF *N*-BENZOYL-*N*-PHENYLHYDROXYLAMINE

$(n\text{-}C_8H_{17})_2$Sn-[ON(Ph)COPh]$_2$ IR (liquid)	Ph_2Sn[ON(Ph)COPh]$_2$ IR (solid) [a]	$(n\text{-}C_4H_9)$Sn-[ON(Ph)COPh]$_3$ IR (solid) [a]	Assignment
3100vvw(sh)			(m + k)
3073w	3064mw		ν(C—H)z_1
	3050mw(sh)		ν(C—H)z_3
2963s			ν(C—H) octyl
2931vvs	2938mw		ν(C—H) octyl; phenyl mode
2877m(sh)			ν(C—H) octyl
2852s	2857w		ν(C—H) octyl; phenyl mode
1953vvw(br)	1958vvw(br)	1958vvw(br)	
1882vvw(br)	1882vvw(br)	1881vvw(br)	
1806vvw(br)	1812vvw(br)	1810vvw(br)	
	1752vvw(br)	1751vvw(br)	Combinations
		1700vvw(br)	
1688vvw(br)		1668vvw(br)	
1600m(sh)	1604w(sh)	1600ms(sh)	ν(C—C)k
1586vs	1588s	1586vs	ν(C—C)l
		1561vs(sh)	
1547vvs	1545vs(sh)		ν(C=O)
		1536vvs(br)	

TABLE 7 (Continued)

$(n\text{-}C_8H_{17})_2Sn$-[ON(Ph)COph] IR (liquid)	$Ph_2Sn[ON(Ph)COPh]_2$ IR (solid)[a]	$(n\text{-}C_4H_9)Sn$-$[ON(Ph)COPh]_3$ IR (solid)[a]	Assignment
	1530vvs		
	1516vvs		
1494s		1493vs(sh)	
	1483ms(sh)		ν(C—C)m
1460ms	1461s		ν(C—C)n
1446ms(dbt)	1443vs(sh)		
1435ms(dbt)	1430vs		ν(C=N)
1417mw(sh)			δ_a(C—H)
1377vw			
1357w			
	1333vw		ν(C—C)o
1312vw(br)	1313vw	1315mw(br)	ν(C—C)o
1294vw	1297w	1294mw(sh)	β(C—H)e
1280vvw(br)	1284vvw(sh)		
1260vvw	1264vw	1262vw(sh)	X-sens. q
	1184vw(sh)		β(C—H)a
1160m	1162m(sh)	1160ms	
1154mw(sh)	1155m		β(C—H)c
1101vvw(br)	1100vvw		
1076mw	1078m	1077mw	β(C—H)d
1040m	1043ms	1042s	
1018ms	1020s	1018s	β(C—H)b
1002w	1006w	1003m(sh)	Ring p
970vvw	973vw		γ(C—H)h
936s	941vs		ν(N—O)
930s(sh)	920m		
		868vw	
844vvw(br)	852vvw(br)	848vw(br)	
834vvw(br)			γ(C—H)g
778ms	780s(sh)		X-sens. r
768ms	774s	771vs	
	734s		
720m	726m	723s(sh)	γ(C—H)f
693vvs	697vvs	693vvs	ϕ(C—C)v
666s	670s	668s	
	664w(sh)		
	660vw(sh)		
617vw	621vw	618w	α(C—C—C)s
602w	608w	605mw	Ligand vibration and γ(Sn—C) butyl
578vvw			
	570w(sh)	567w	
	559mw		
542w(br)		550mw	ν_a(Sn—O)
	515w	510w(sh)	
		506w	
496w			
	486vw		
		479vvw(br, sh)	
	457m		
	448ms		
		440ms	ν_a(Sn—O)
433mw			
	408vvw(br)		ϕ(C—C)w
392mw			
383vvw	370vvw(br)		
360vvw			
348vvw			
	298vvw(br)		
	270m		
		260w	ν(Sn—C(Phenyl))
	254m(sh)		X-sens. u

[a] Recorded as nujol and halocarbon mulls.

TABLE 8

VIBRATIONAL SPECTRA OF $(CH_3)_2Sn[ON(CH_3)COCH_3]_2$

IR [a]	Raman [b]	Assignment
3015w	3005vw	ν_a(C—H)Sn
2990w	2975vw	ν_a(C—H)
2944w	2933s	ν_s(C—H)Sn
1609vvs	1606w	ν(C=O)
1486vw	1482m	
	1474m	
1458m	1453s	
1428s	1422m(sh)	ν(C—N)
1397w	1398w	δ_a(C—H)Sn
1366w	3169	
1230		
1182vw	1184w	δ_s(C—H)Sn
1162s		
1156s		
1035w	1035w	
	1023w	
974s	970w(br)	ν(N—O)
966s	961w(br)	
805w(sh)		
784m(br)		$\rho(CH_3$—Sn)
751vvs	756vw	
681vvw		
630vs	622vw	
602mw		
	595vvw	
571s	563w	ν_a(Sn=C)
550m	556vw(sh)	ν_a(Sn=O)
518vw	515vvs	ν_s(Sn—C)
495w	491vw	ν_a(Sn—O)?
481mw		
	260vw	
	208vvw	
	169w	
	120vvw	

[a] Recorded on nujol and halocarbon mulls. [b] Compacted powder.

group theory to an ideal *cis*-$(CH_3)_2Sn[O]_4$ octahedral species predicts two normal tin—carbon stretching modes, A_1 and B_1, which will be both infrared and Raman active, although the A_1 mode should be polarised in the Raman. The free hydroxylamine has a single intense band (584 cm^{-1}) in the infrared in this region, although there is no sign of a corresponding band in the complex. The three bands in the infrared of the complex (605, 532 and 517 cm^{-1}) are intense, reflected in the Raman by two intense bands (533 and 522 cm^{-1}) and a very weak band (606 cm^{-1}). The absorption at higher wavenumber is above the limits normally observed for tin—methyl stretching modes, although there exists only one other precedent, namely *cis*-octahedral $(CH_3)_2Sn(oxin)_2$, where an absorption at 593 cm^{-1} was tentatively assigned as a tin—carbon stretching mode, the other tin—carbon stretching mode being hidden by ligand vibrations [22]. Assignment of the other two bands (532 and 517 cm^{-1}) to tin—carbon stretching modes places the wavenumber difference as unusually small, and places the sym-

TABLE 9

VIBRATIONAL SPECTRA OF $(CH_3)_2Sn[ON(H)COCH_3]_2$

IR [a]	Raman [b]	Assignment
3182vvs		ν_a(N—H)
3106vs		ν_s(N—H)
3019vvs		ν_a(C—H)
	3003vvw	
3000vvs	2998vvw	ν_s(C—H)
	2978vvw	
	2932w	
2920vs	2920vw(sh)	ν_a(C—H)
	2880vvw	
	2857vvw	
2848vs	2848vvw	ν_s(C—H)
2780s	2762vvw	
2768s	2762vvw	
2720ms	2726vvw	
2670ms		
2528vw(br)		
2442vvw(br)		
2346vw		Combinations
2186vvw(br)		
2142vvw		
2058vvw(br)		
1923vvw		
1761vvw(br)		
1697vvw(br)		
1608vvs		ν(C=O)
	1545vvw	
1531vvs		δ(N—H)
1438vvs		
1433vs(sh)	1428vvw	
1422vs		ν(C=N)
1388vs	1391w	$\delta_a(CH_3)Sn$
1343vvs	1350vw	
1332vs(sh)	1333vvw	
1213vw		
1183ms	1188mw	$\delta_s(CH_3)Sn$
1178m		
1101vvs	1098vvw	
1039ms	1042vvw	
982vvs	992mw	ν(N—O)
782vs(br)		$\rho(CH_3—Sn)$
749s(sh)		
697m		
	674vw	
670vvs	669vvw(sh)	
605vs	606vvw	ν_a(Sn—C)
532vvs	533vvs	ν_s(Sn—C)
517vvs	522s	ν(Sn—O)
	486vvw	
436s	438vvw	
429m(sh)	427vvw	
401vvw		
	337vvw	
292vvs	294w	
297m(sh)	238vvw	
	178m	
	149ms	
	115vw(sh)	
	106vw	

[a] Halocarbon and nujol mulls. [b] Compacted powder.

metric mode as less intense than the antisymmetric mode in the Raman. Thus a better fit is obtained if the band at 605 cm^{-1} as assigned to antisymmetric mode and that at 532 cm^{-1} to the symmetric mode.

The tin—carbon stretching region of $(n\text{-}C_8H_{17})_2Sn[O(Ph)COPh]_2$ (Table 7) contains three bands, although in the absence of Raman or comparative data these cannot be assigned with any certainty.

The infrared spectrum of $Ph_2Sn[ON(Ph)COPh]_2$ has also been recorded (Table 7). The tin—carbon(phenyl) stretching modes for various diphenyltin compounds, have been assigned by Poller and coworkers to bands occurring in the 200—300 cm^{-1} region. The symmetric mode occurring below 250 cm^{-1} and consequently out of the range studies here, whilst the antisymmetric mode was observed in the range 267—287 cm^{-1}. This suggests assignment of the absorption at 270 cm^{-1} as the antisymmetric tin—carbon (phenyl) stretching mode.

The mass spectra of $(CH_3)_2Sn[ON(CH_3)COCH_3]_2$ (Table 10) and $(CH_3)_2Sn$-$[ON(Ph)COPh]_2$ (Table 11) show weak parent ions and have base peaks corresponding to the loss of one chelating group, in contrast to $(CH_3)_3Sn[ON$-$(CH_3)COCH_3]$, where loss of one methyl group is the most favourable fragmentation. This indicates the relative stability of the $(CH_3)_2Sn$ moiety in the dimethyltin compounds. Both spectra show ions arising from chelate ring contractions, through loss of an oxygen atom or a nitrene species, discussed in the case of $(CH_3)_3Sn[ON(CH_3)COCH_3]$, although in the present cases, the occurence of these

TABLE 10

THE MAJOR FRAGMENTS IN THE MASS SPECTRUM OF $(CH_3)_2Sn[ON(CH_3)COCH_3]_2$ [a,b]

m/e	Relative intensity [c]	Assignment
325	0.63	$(CH_3)_2Sn[ON(CH_3)COCH_3]_2^+$
310	16.98	$(CH_3)Sn[ON(CH_3)COCH_3]_2^+$
295	0.40	$Sn[ON(CH_3)COCH_3]_2^+$
294	0.42	$(CH_3)Sn[ON(CH_3)COCH_3][N(CH_3)COCH_3]^+$
281	1.21	$(CH_5)Sn[ON(CH_3)COCH_3][O_2CCH_5]^+$
237	100.00	$(CH_3)_2Sn[ON(CH_3)COCH_3]^+$
221	1.51	$(CH_3)_2Sn[N(CH_3)COCH_3]^+$
207	48.84	$Sn[ON(CH_3)COCH_3]^+$
191	1.84	$Sn[N(CH_3)COCH_3]^+$
178	12.79	$Sn[O_2CCH_3]^+$
166	1.63	
164	*d*	$Sn[ONCH_3]^+$
150	*d*	$Sn[OCH_3]^+$
149	*d*	$(CH_3)_2Sn^+$
136	11.86	$Sn[OH]^+$
134	*d*	$(CH_3)Sn^+$
120	*d*	SnH^+
119	*d*	Sn^+
89	2.32	$HON(CH_3)COCH_3^+$
88	0.69	$ON(CH_3)COCH_3^+$
73	9.07	$ONCO(CH_3)^+$
71	1.16	
58	4.88	$ON{=}CO^+$
56	20.23	

[a] Mass count based on ^{119}Sn. [b] Direct insertion at 140°C. [c] Based on the most intense tin containing fragment. [d] Overlay of peaks.

TABLE 11

THE MAJOR FRAGMENTS IN THE MASS SPECTRUM OF $(CH_3)_2Sn[ON(Ph)COPh]_2$ [a,b]

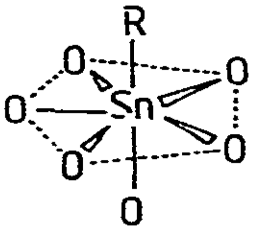
m/e	Relative intensity [c]	Assignment
573	0.06	$(CH_3)_2Sn[ON(Ph)COPh]_2^+$
558	12.50	$(CH_3)Sn[ON(Ph)COPh]_2^+$
542	2.03	$(CH_3)Sn[N(Ph)COPh][ON(Ph)COPh]^+$
526	0.19	
479	0.56	
467	13.59	$(CH_3)Sn[ON(Ph)COPh][O_2CPh]^+$
451	2.03	$(CH_3)Sn[N(Ph)COPh][O_2CPh]^+$
424	0.80	
406	0.34	
381	1.47	
376	1.25	
361	100.00	$(CH_3)Sn[ON(Ph)COPh]^+$
345	5.00	$(CH_3)_2Sn[N(Ph)COPh]^+$
331	20.31	$Sn[ON(Ph)COPh]^+$
313	3.28	
287	3.44	
270	16.25	$(CH_3)_2Sn[O_2CPh]^+$
255	1.63	$(CH_3)Sn[O_2CPh]^+$
240	13.91	$Sn[O_2CPh]^+$
226	10.62	$Sn[ONPh]^+$
212	4.38	$Sn[OPh]^+$
197	125.00	$HN(Ph)COPh^+$
180	39.06	
166	10.31	$(CH_3)_2SnOH^+$
151	1.88	$(CH_3)SnOH^+$
136	6.25	$SnOH^+$
119	2.97	Sn^+
105	[d]	$PhCO^+$

[a] Mass count based on ^{119}Sn. [b] Direct insertion at 160°C. [c] Based on the most intense tin containing fragment. [d] Off scale.

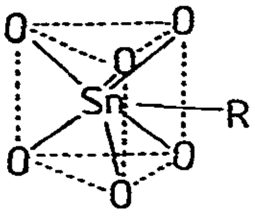
ions are more frequent. The majority of the other ions in the mass spectra of these two compounds correspond to the stepwise stripping of substituents.

(iii) O-n-Butyltin tris-N-benzoyl-N-phenylhydroxylamine. The solid-state indrared spectrum of $(n\text{-}C_4H_9)Sn[ON(Ph)COPh]_3$ (Table 7) shows a single carbonyl stretching frequency (1547 cm^{-1}) which is again substantially lowered in comparison to that of the free hydroxylamine, and there is no indication of a free carbonyl or hydroxyl group vibration, suggesting that the three hydroxylamine residues are equivalent and bidentate, thus making the tin atom seven-coordinated. The QS value of this compound (2.05 mm sec^{-1}) is lower than that of the *trans*-six-coordinate $(n\text{-}C_4H_9)_2Sn[ON(Ph)COPh]_2$ and the trialkyltinhydroxylamine derivatives. The low IS (0.76 mm sec^{-1}), which indicates a low *s*-electron density at the tin nucleus can be interpreted in terms of increased shielding of the *s*-electrons by a greater involvement of the *d*-electrons as the coordination number is increased from five or six to seven. The QS of the seven-coordinate $(n\text{-}C_4H_9)Sn(oxin)_3$ has the value, 1.82 mm sec^{-1} (IS 0.69 mm sec^{-1}), and has been interpreted on a point charge basis in terms of the two-coordinate geometries, pentagonal bipyramidal XXIII and the $[TaF_7]^{2-}$ type structure

XXIV derived from a trigonal prism by addition of a seventh ligand on the normal to one face, however distinction between the two structural types was not possible [24]. However, the similarity between the Mössbauer parameters of the oxinate and (n-C_4H_9)Sn[ON(Ph)COPh]$_3$, suggests a similar seven-coordinate geometry, although distinction between the two geometries XXIII and XXIV, which a small extent of distortion would reduce to a question of semantics, is not possible. Both possible seven-coordinate structures, can be expected to give a single tin—carbon stretching mode in the infrared and there appear to be several possibilities in the spectrum of n-butyltintris-*N*-benzoyl-*N*-phenylhydroxylamine (Table 9). However, on the basis of the previously assigned infrared spectra of n-butyltin complexes [21] the absorption at 605 cm^{-1} is best assigned to this mode.



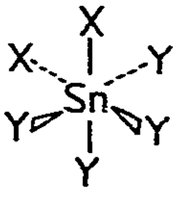
(XXIII)



(XXIV)

(iv) O-Dihalogenotin bis-hydroxylamines. The Mössbauer spectra of the four compounds Cl_2Sn[ON(Ph)COPh]$_2$, Br_2Sn[ON(Ph)COPh]$_2$, I_2Sn[ON(Ph)COPh]$_2$ and Cl_2Sn[ON(CH_3)$COCH_3$]$_2$ all exhibit single resonances, with zero QS values (Table 1). The three derivatives of *N*-benzoyl-*N*-phenylhydroxylamine have an approximately inverse linear relationship between the electronegativity of the halogen substituent and the observed IS value. Similar relationships have been observed before, and can be attributed to the increase of the positive change induced on the tin atom as the substituents become more electronegative, which reduces the valence shell electron density, particularly from the *s*-orbital leading to a decrease in the IS.

The physical and spectroscopic properties of the analogous dihalogenotin bisacetylacetonates have been extensively studied and their structure assigned as *cis*-X_2SnY_4 octahedral XXV on the basis of these properties and dipole moments data [25]. A recent study by Bancroft and Sham [26] has reported the Mössbauer spectrum of dichlorotin bisacetylacetonate, and shown that the compound has a small QS value (IS 0.15 mm sec^{-1} and QS 0.54 mm sec^{-1}) in contrast to previous reports, where the spectrum was not as well resolved (IS 0.25 mm sec^{-1} and QS 0 mm sec^{-1}). This value is similar to the values observed for Cl_2Sn[ON(Ph)COPh]$_2$ (IS 0.41 mm sec^{-1}, QS 0 mm sec^{-1}) and Cl_2Sn[ON(CH_3)$COCH_3$]$_2$ IS 0.35 mm sec^{-1}, QS 0 mm sec^{-1}), although no resolvable QS was observed.



(XXV)

The molecular structure of Cl_2Sn[ON(Ph)COPh]$_2$ has been investigated and the compound shown to have the *cis*-X_2SnY_4 octahedral structure XXV with a chlorine—tin—chlorine bond angle of 98.7° [5]. Since the Mössbauer data for the dibromotin, diiodotin, and dichlorotin derivatives vary linearly with the electronegativity of the halogen, both $Br_2Sn[ON(Ph)COPh]_2$ and $I_2Sn[ON(Ph)COPh]_2$ can also be assigned the *cis* structure.

A comparison of the vibrational spectra of the compounds $X_2Sn[ON(Ph)COPh]_2$ for X = Cl, Br and I, is given in Table 12 and that of $Cl_2Sn[ON(CH_3)COCH_3]_2$ in Table 13. The carbonyl stretching frequencies are again lowered in comparison with the respective free hydroxylamines, indicating the bidentate nature of the hydroxylamine residue. The normal tin—halogen stretching modes for an ideal *cis*-X_2SnY_4 octahedral species, as predicted by group theory, are one A_1 and one B_1 mode, both of which are infrared and Raman active. The intense band at 322 cm^{-1} in the Raman spectrum of $Cl_2Sn[ON(Ph)COPh]_2$ is readily assigned to the A_1(Sn—Cl) stretching mode, and appears in the infrared at 325 cm^{-1}; the adjacent band in the infrared at 333 cm^{-1} is of medium intensity and can be assigned to the B_1 mode. The analogous vibrations in $Cl_2Sn[ON(CH_3)COCH_3]_2$ appear with a slightly larger separation at 326 and 342 cm^{-1} in the infrared (Raman 330 and 349 cm^{-1}). The infrared spectra of $Cl_2Sn[acac]_2$ in solution and solid-phase, has been recorded by Jones and Fay [25] and they assigned a broad absorption at 334 cm^{-1} (solid-phase) to the Sn—Cl stretching modes. This represents quite reasonable agreement, which is to be expected since both the acetylacetonate and hydroxylamine derivatives are assigned the *cis*-octahedral structure, and both ligands involve bonding through two oxygen atoms to the tin atom. However Okawara and coworkers [28] have assigned bands at 318 and 284 cm^{-1} to the tin—chlorine stretching frequencies in dichlorotin bis-*N*,*N*-dimethyldithiocarbamate. The symmetric tin—bromine stretching vibration (A_1) is assigned to the Raman intense absorption at 171 cm^{-1}, and the antisymmetric vibration (B_1) to that at 270 cm^{-1} in both Raman and infrared for $Br_2Sn[ON(Ph)COPh]_2$ Jones and Fay [25] assigned a tin—bromine stretch to the absorption at 264 cm^{-1} in the infrared spectrum of $Br_2Sn[acac]_2$, and also observed a weak band at 177 cm^{-1}, which they did not assign, suggesting that there may be a similarity again between the hydroxylamine and acetylacetonate derivatives, although in the absence of Raman data for the acetylacetonates, the assignment of the 177 cm^{-1} band must remain tentative. Similarly for $I_2Sn[ON(Ph)COPh]_2$, the symmetric tin—iodine stretch (A_1) is obvious in the Raman at 149 cm^{-1} and the antisymmetric mode (B_1) mode is best assigned to the band at 186 cm^{-1} in the Raman. This partially agrees with the assignment of Fay and Jones [25] of the band at 185 cm^{-1} in the infrared of $I_2Sn[acac]_2$, to the tin—iodine stretch, although they also assigned a band in the solid-state spectrum, at 174 cm^{-1}, to this vibration.

The mass spectra of $Cl_2Sn[ON(CH_3)COCH_3]_2$ (Table 14), $Cl_2Sn[ON(Ph)COPh]_2$ (Table 15) and $Br_2Sn[ON(Ph)COPh]_2$ (Table 16) have been recorded, and as might be expected are generally similar. The major fragments of $Cl_2Sn[ON(CH_3)COCH_3]_2$ again show ions arising from the ring contraction mechanisms, as observed previously for the dialkyltin and trialkyltin hydroxylamine derivatives. An ion at *m/e* 261 results from the loss of oxygen by a contraction of the five-membered heterocyclic chelate ring, however several ions (*m/e* 301, 291, 232 and 178) result from the ring contraction by loss of the nitrene species [$:NCH_3$]; this mechanism appearing to be more favourable than the loss of oxy-

TABLE 12

VIBRATIONAL SPECTRA OF $X_2Sn[ON(Ph)COPh]_2$ (X = Cl, Br, I)

$Cl_2Sn[ON(Ph)COPh]_2$		$Br_2Sn[ON(Ph)COPh]_2$		$I_2Sn[ON(Ph)COPh]_2$		Assignment
IR ^{a}	Raman ^{b}	IR ^{a}	Raman ^{b}	IR ^{a}	Raman ^{b}	
3073vw	3066vw	3069vw		3070vw		ν(C—H)z_1
3030vvw		3030vw				ν(C—H)z_3
1979vvw(br)		1960vvw(br)		1967vvw(br)		
1905vvw(br)		1930vvw(br)				
1886vvw(br)				1895vvw(br)		
1818vvw(br)				1824vvw(br)		Combinations
1774vvw(br)				1753vvw(br)		
1701vvw(br)				1702vvw(br)		
1600mw	1602vvs	1601w(sh)	1599vs	1604w	1602vs	ν(C—C)k
1593w		1597w				
1585mw		1587m		1586ms		ν(C—C)k
1526vvs		1528vs	1528w	1526vvs	1538s	
1514vvs	1510m	1512vvs	1510mw	1517vvs	1505s	
1500vvs		1498vvs	1504w	1502vvs		ν(C—C)m
1468ms	1465w	1469m	1464vw	1461s		ν(C—C)n
1441vs	1442ms	1438vvs	1443m	1443vs	1450vs	ν(C=N)
1396vvw		1395vvw		1400vvw		Combin. (u + v)
1321vvw		1318vw(br)		1318mw		ν(C—C)o
1299vvw		1300vw				β(C—H)e
	1294vvw			1284mw	1282s	X sens. q.
1268vvw(sh)	1276m	1273vvw(br)	1273mw			
	1228m		1227m			
1174vw	1181vw	1175vw	1183vw	1170vw		β(C—H)a
1153mw	1152mw	1153m	1153vw	1154vs	1160s	β(C—H)c
1103vvw		1100vvw(br)				Comb. (v + w)
1080w		1088w		1075ms		β(C—H)d
1040mw		1040m		1038ms		
	1031vw		1030vw			
1018ms		1019s		1017vs		β(C—H)b
1003vw	1000vs	1005w	1001vvs	1002ms	1002vs	Ring p
975vvw(br)		975vw		976vw		γ(C—H)h
940ms	937vvw	941s	936vvw	939vs		
931m		932s		931ms		ν(N—O)
919mw		921m		920vs		
850vvw(br)	850vw	851vvw	850vvw	852vw		γ(C—H)g
836vvw(br)				842vw		
805vvw				807vvw		
783mw(sh)	783vw	786mw(sh)	784vw			X-sens. r
774s	776vw	775vvs		777vvs		
723mw	724vw	727ms	724vw	721s		γ(C—H)f
707s	708vvw	708vvs	710vw	708vs		
698ms		698vs				
694ms		694vs		694vvs		ϕ(C—C)v
691ms(sh)						
670mw		673m		671s		
623w(dbt)	623w(sh)	623w(sh)				
619w(dbt)		621mw		620w(sh)		α(C—C—C)s
616w(sh)	617m	616mw	615w		620m	
	607m		603w	608m	608m	
	586vw	590w	583vw	580s	580s	
558w		530w				
516vvw	512mw		512vw	517mw		
493vvw	490vvw	499vvw		492vvw		X-sens. y
479vvw		487vvw		478vw		
451w	447vvw	449s	448vw	450vs		ν_a(Sn—O)
443mw				436mw(sh)		

TABLE 12 (Continued)

$Cl_2Sn[ON(Ph)COPh]_2$		$Br_2Sn[ON(Ph)COPh]_2$		$I_2Sn[ON(Ph)COPh]_2$		Assignment
IR [a]	Raman [b]	IR [a]	Raman [b]	IR [a]	Raman [b]	
375vvw		380vw		372mw		
333mw		333vw				ν_a(Sn—Cl)
325m	322ms					ν_s(Sn—Cl)
		312vvw				
		299vvw		289vvw(sh)		X-sens. t
	265vvw	270vw	270vw	262mw		ν_a(Sn—Br)?
	249mw		244vw			
	218vw		217mw		218s	
	176vw		176vw(sh)		186s	
			171vs			ν_s(Sn—Br)
	150w		145w			
					149vs	ν_s(Sn—I)
					108s	
					95s	

[a] Infrared spectra recorded as nujol and halocarbon mulls. [b] Raman spectra recorded as compacted solids.

gen, which only occurs for contraction of the base ion $Cl_2Sn[ON(CH_3)COCH_3]^+$. The fact that the base ion corresponds to the loss of one hydroxylamine group suggests that the Cl_2Sn group is quite stable, although it would appear from the fragments, *m/e* 242, and 207, that removal of one chlorine atom greatly facilitates the subsequent removal of the second.

In the mass spectrum of $Br_2Sn[ON(Ph)COPh]_2$, the parent ion is comparatively weak and the base peak at *m/e* 331 corresponds to the ion Sn[ON-Ph)(Ph)COPh]$^+$, whilst in the mass spectrum of $Cl_2Sn[ON(Ph)COPh]_2$ the parent ion corresponds to the base peak, and the ion Sn[ON(Ph)COPh]$^+$ is only the seventh most intense fragment. This indicates the relative ease in which the bromo compound is broken up under electron impact, whilst the chloro compound appears more stable. Again fragments arising from ring contraction via loss of oxygen are apparent in both spectra, although the contractions via loss of the nitrene species [:NPh] are far more common in the spectrum of Cl_2Sn-$[ON(Ph)COPh]_2$ giving rise to some very intense peaks (*m/e* 487 and 240), whilst they are less evident in the spectrum of $Br_2Sn[ON(Ph)COPh]_2$. The major process in the bromo derivative appears to be decarboxylation of the heterocyclic chelate ring, yielding ions containing the diphenylamino group, and giving rise to relatively abundant fragments (*m/e* 657, 641, 578 and 562). Such a rearrangement involves the (1,2) migration of a phenyl group, and the formation of a tin—nitrogen interaction. However, the dichloro derivative shows no evidence for an analogous rearrangement.

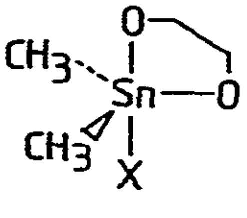
(v) O-Dimethylhalogenotin hydroxylamines. The greatly reduced value of the carbonyl stretching vibration (ca. 1530 cm^{-1}) for the *O*-dimethylhalogenotin hydroxylamines, $(CH_3)_2Sn(X)[ON(Ph)COPh]$ (X = Cl, Br, I) (Table 17) is unequivocal evidence for the bidentate nature of the hydroxylamine ligand and five-coordinated tin in these derivatives. On the basis of Bent's rule [15], the most probable geometry would be XXVI, in which the second axial site is occupied by the halogen atom.

TABLE 13

VIBRATIONAL SPECTRA OF $Cl_2Sn[ON(CH_3)COCH_3]_2$

IR [a]	Raman [b]	Assignment
3047vvw		
3017vvw	3010vw	ν_a(C—N)
2967vvw(br)	2961m	ν_s(C—H)
	2941mw	
2569vvw(br)		
2409vvw(br)		
2357vvw(br)		
2187vvw(br)		
	2078vvw	
	2058vvw	Combination
1973vvw(br)	1975mw	
	1960mw	
1930vvw(br)		
1780vvw(br)		
1722vvw(br)		
1602vvs	1606ms	ν(C=O)
1511w		
1468s		
1451s	1453s	
1424ms	1422m	ν(C=N)
1395m		
1372ms	1375vw	
	1232vvw	
1224w	1223vw	
1207vvw(br)		
1164m		
	1066w	
1033w	1036w	
969ms	966vw(br)	ν(N--O)
	947vw(br)	
804vw		
757vs	758w	
723vvw		
606mw	643vw	
686mw		
595w	558m	
520vw		ν(Sn—O)
342m	349ms	ν_a(Sn—Cl)
326ms	330vvs	ν_s(Sn—Cl)
314mw		
303vw		
206vvw(br)	270mw	

[a] Recorded as nujol and halocarbon mulls. [b] Compacted powder.



(XXVI)

Mössbauer data for these derivatives are listed in Table 1, and, like the dihalogenotin bis-hydroxylamine derives, the IS values increase with decreasing electronegativity of the halogen substituent. The QS however, decreases with decreas-

TABLE 14

THE MAJOR FRAGMENTS IN THE MASS SPECTRUM OF $Cl_2Sn[ON(CH_3)COCH_3]_2$ [a,b]

m/e	Relative intensity [c]	Assignment
365	16.82	$Cl_2Sn[ON(CH_3)COCH_3]_2^+$
344	1.26	
330	51.60	$ClSn[ON(CH_3)COCH_3]_2^+$
301	0.84	$ClSn[ON(CH_3)COCH_3][O_2CCH_3]^+$
291	1.47	$Cl_2Sn[O_2CCH_3]_2^+$
277	100.00	$Cl_2Sn[ON(CH_3)COCH_3]^+$
261	1.11	$Cl_2Sn[N(CH_3)COCH_3]^+$
242	17.88	$ClSn[ON(CH_3)COCH_3]^+$
232	7.89	$Cl_2Sn[O_2CCH_3]^+$
207	53.70	$Sn[ON(CH_3)COCH_3]^+$
178	7.37	$Sn[O_2CCH_3]^+$
154	22.10	$ClSn^+$
136	10.00	$SnOH^+$
119	4.22	Sn^+
89	13.17	$HON(CH_3)COCH_3^+$
88	78.90	$ON(CH_3)COCH_3^+$
73	37.90	$ONCO(CH_3)^+$
58	16.32	$ONCO^+$
56	49.45	$N(CH_3)C(CH_3)^+$
43	[d]	$OCCH_3^+$
36	41.15	HCl^+

[a] Based on ^{119}Sn and ^{35}Cl. [b] Direct insertion at 140°C. [c] Based on the most intense tin-containing fragment. [d] Off scale.

ing electronegativity of the halogen, although in both cases the changes are small. The QS values of the dimethylhalogenotin *N*-benzoyl-*N*-phenylhydroxylamines are marginally larger than that of the corresponding trimethyltin derivative, which was assigned the *cis*-R_3SnL_2 trigonal bipyramidal structure. Such a small increase in QS is in keeping with the $(CH_3)_2Sn(X)[ON(Ph)COPh]$ compounds having a structure of type XXVI, since replacement of one methyl group of the trimethyltin derivative by a more electronegative halogen would clearly result in a greater imbalance in the σ-electron framework, resulting in a larger QS value.

A more quantitative point charge approach has been adopted by Ruddick and Sams [24] to interpret the structure of $(CH_3)_2Sn(Cl)[oxin]$, which they proposed as trigonal bipyramidal with equatorial methyl groups and an axial chlorine atom (similar to XXVI, although they found the sign of the QS depended on the carbon—tin—carbon bond angle. A Mössbauer study of the compounds $(C_2H_5)_2Sn(X)[oxin]$, where X = Cl, Br and I [22], shows similar relationships between the IS and QS, and the halogen electronegativity to those observed for the dimethyl halogenotin *N*-benzoyl-*N*-phenylhydroxylamines. On the basis of the similarity of the QS for the three compounds (2.85—3.13 mm sec^{-1}), the possibility of an associated structure through bridging halogen atoms, was discounted as iodine could not be expected to exhibit bridging to the same extent as chlorine, and any major structural differences would have been reflected in the values of the QS. Thus the compounds were assigned a trigonal bipyramidal structure, although no distinction was made between the various possible isomers.

TABLE 15

THE MAJOR FRAGMENTS IN THE MASS SPECTRUM OF $\mathrm{Cl_2Sn[ON(Ph)COPh]_2}$ [a,b]

m/e	Relative intensity [c]	Assignment
613	100.0	$\mathrm{Cl_2Sn[ON(Ph)COPh]_2^+}$
597	2.77	$\mathrm{Cl_2Sn[ON(Ph)COPh][N(Ph)COPh]^+}$
578	32.30	$\mathrm{ClSn[ON(Ph)COPh]_2^+}$
562	0.92	$\mathrm{ClSn[ON(Ph)COPh][N(Ph)COPh]^+}$
522	6.00	$\mathrm{Cl_2Sn[ON(Ph)COPh][O_2CPh]^+}$
506	16.15	$\mathrm{Cl_2Sn[N(Ph)COPh][O_2CPh]^+}$
487	74.00	$\mathrm{ClSn[ON(Ph)COPh][O_2CPh]^+}$
471	33.82	$\mathrm{ClSn[N(Ph)COPh][O_2CPh]^+}$
445	2.15	$\mathrm{Cl_2Sn[ON(Ph)COPh][CO_2]^+}$
436	1.23	
401	96.85	$\mathrm{Cl_2Sn[ON(Ph)COPh]^+}$
385	*d*	$\mathrm{Cl_2Sn[N(Ph)COPh]^+}$
366	72.35	$\mathrm{ClSn[ON(Ph)COPh]^+}$
350	3.85	$\mathrm{ClSn[N(Ph)COPh]^+}$
331	38.50	$\mathrm{Sn[ON(Ph)COPh]^+}$
315	2.30	$\mathrm{Sn[N(Ph)COPh]^+}$
261	5.80	$\mathrm{ClSn[ONPh]^+}$
240	61.50	$\mathrm{Sn[O_2CPh]^+}$
226	*d*	$\mathrm{Sn[ONPh]^+}$
224	*d*	$\mathrm{Sn[COPh]^+}$
212	7.23	$\mathrm{ON(Ph)COPh^+}$
204	10.45	
197	338.40	$\mathrm{HN(Ph)COPh^+}$
180	20.00	$\mathrm{N(Ph)C(Ph)^+}$
167	33.85	
154	61.52	$\mathrm{ClSn^+}$
136	8.00	$\mathrm{SnOH^+}$

[a] Based on ^{119}Sn and ^{35}Cl. [b] Direct insertion at 180°C. [c] Based on the most intense tin-containing peak. [d] Overlay.

The similar dimethylchlorotin dithiocarbamates have been assigned a tetrahedral structure by Fitzsimmons and Sawbridge [29] on the basis of a semi-quantitative point charge calculation for the Mössbauer parameters. However, $\mathrm{(CH_3)_2Sn(Cl)[S_2CN(CH_3)_2]}$ has been shown to have a distorted trigonal bipyramidal structure, with the two methyl groups occupying the equatorial sites with a sulphur atom, whilst the other sulphur atom of the intramolecular chelating dithiocarbamate group and the chlorine atom occupy the axial sites [30]. The dialkylhalogenotin dithiocarbamates have also been assigned the analogous five-coordinate structure on the basis of PMR and infrared studies [28]. The QS of $\mathrm{(CH_3)_2Sn(Cl)[S_2CN(CH_3)_2]}$ (2.98 mm sec^{-1} [29]) is intermediate between that of the corresponding oxinate (3.12 mm sec^{-1} [22]), and the hydroxylamine (2.71 mm sec^{-1}).

The proton magnetic resonance spectra of the compounds $\mathrm{(CH_3)_2Sn(X)[ON(Ph)COPh]}$, X = Cl, Br and I, in deuterated chloroform all exhibit the expected spin—spin coupling about the tin-methyl protons (Table 2). The individual satellites usually observed for ^{119}Sn and ^{117}Sn, could not be clearly resolved for the bromo and iodo compounds, and so a mean value was estimated for the chloro compound ($^2J(^{119,117}\mathrm{Sn—C—}^1\mathrm{H})$ 77.9 Hz), for comparison with the others. The

TABLE 16

THE MAJOR FRAGMENTS IN THE MASS SPECTRUM OF $Br_2Sn[ON(Ph)COPh]_2$ [a,b]

m/e	Relative intensity [c]	Assignment
701	1.95	$Br_2Sn[ON(Ph)COPh]_2^+$
685	0.48	$Br_2Sn[ON(Ph)COPh][N(Ph)COPh]^+$
657	2.90	$Br_2Sn[ON(Ph)COPh][NPh_2]^+$
641	0.65	$Br_2Sn[N(Ph)COPh][NPh_2]^+$
622	61.30	$Br_2Sn[ON(Ph)COPh]_2^+$
606	4.84	$BrSn[ON(Ph)COPh][N(Ph)COPh]^+$
578	32.30	$BrSn[ON(Ph)COPh][NPh_2]^+$
562	2.26	$BrSn[N(Ph)COPh][NPh_2]^+$
531	4.68	$BrSn[ON(Ph)COPh][O_2CPh]^+$
515	2.58	$BrSn[N(Ph)COPh][O_2CPh]^+$
489	32.30	$Br_2Sn[ON(Ph)COPh]^+$
471	2.74	
443	22.60	
410	9.78	$BrSn[ON(Ph)COPh]^+$
394	5.17	$BrSn[N(Ph)COPh]^+$
366	10.95	
358	3.87	
331	100.00	$Sn[ON(Ph)COPh]^+$
315	71.00	$Sn[N(Ph)COPh]^+$
240	30.65	$Sn[O_2CPh]^+$
212	11.30	$ON(Ph)COPh^+$
197	*d*	$HN(Ph)COPh^+$
179	9.04	
167	64.50	
154	10.33	
136	6.13	$SnOH^+$
122	87.20	$PhCO_2H^+$
119	12.90	Sn^+

[a] Based on ^{119}Sn and ^{79}Br. [b] Direct insertion at 180°C. [c] Based on the most intense tin-containing fragment. [d] Off scale.

$^2J(^{119,117}Sn—C—^1H)$ values of these compounds (X = Cl, 77.9 Hz; X = Br, 76.5 Hz; and X = I, 73.4 Hz) are of the same order, and slightly larger than the value (71 Hz) expected for methyltin species, with the alkyl groups located in an sp^2 hybridised arrangement about the tin [31]. Such a small increase can be interpreted in terms of redistribution of *s*-electron density within the hybrid set, away from the hybrid orbital to the electronegative substituent (oxygen or halogen) and into the remaining two sp^2 hybrids orientated towards the methyl groups, accompanied by the reciprocal reorientation of the *p*-electron density. Alternatively the perturbation from ideal sp^2 tin—methyl behaviour can be explained in terms of widening of the carbon—tin—carbon bond angle, such that it is distorted towards a linear arrangement. The distortion, however, must be small, since a linear species is expected to give rise to spin—spin coupling constants of ca. 100 Hz. The $^2J(^{119}Sn—C—^1H)$ value of $(CH_3)_2Sn[ON(CH_3)COCH_3]_2$ was 81.5 Hz, slightly larger than the values observed here, and the solid-state structure of this compound shows it to have a carbon—tin—carbon bond angle of 145.8° [4]. It is interesting to note that if the coupling is an indirect measure of the distortion of the methyl—tin—methyl bond angle away from ideal sp^2 towards linearity, the coupling constants of the dimethylhalogenotin hydroxyl-

(Continued on p. 47)

TABLE 17

VIBRATIONAL SPECTRA OF CH$_3$)Sn(X)[ON(Ph)COPh] (X = Cl, Br, I)

(CH$_3$)$_2$Sn(Cl)[ON(Ph)COPh]		(CH$_3$)$_2$Sn(Br)[ON(Ph)COPh]		(CH$_3$)$_2$Sn(I)[ON(Ph)COPh]		Assignments
IR [a]	Raman [b]	IR [a]	Raman [b]	IR [a]	Raman [b]	
3114vvw(br)				3108vvw(br)		(m + k)
3080vvw(sh)						ν(C—H)z$_4$
3074w	3072vw	3068vvw	3072vvw	3068vw	3068vvw	ν(C—H)z$_1$
3043vvw(sh)						ν(C—H)z$_3$
3009vvw(br)	3008vvw	3002vvw(br)	3007vvw(br)	3009vvw(br)	3010vvw(br)	ν_a(C—H)Sn)
					2984vvw	(m + n)
2924vw(br)	2930vvw	2920vvw(br)	2927vvw	2922vvw	2932vvw	ν_s(C—H)Sn)
					2879vvw(br)	(k + q) combin.
1980vvw(br)						
1966vvw(br)		1964vvw(br)		1965vvw(br)		
1894vvw(br)		1896vvw(br)		1894vvw(br)		
1823vvw(br)		1822vvw(br)	1816vvw(b	1816vvw(br)		
1810vvw(br)		1808vvw(br)		1807vvw(br)		Combinations
1760vvw(br)		1755vvw(br)		1768vvw(br)		
				1746vvw(br)		
1721vvw(br)		1713vvw(br)		1713vvw(br)		
1633vvw(br)						
1616vvw(br)		1614vvw(br)		1613vvw(br)		
1601mw(sh)	1602s	1600vw(sh)	1603s	1599w(sh)	1604s	ν(C—C)k
1590ms(sh)		1588w(sh)		1590mw(sh)		
1584vs	1585w(sh)	1582m	1585w(sh)	1582ms	1583w(sh)	ν(C—C)1
				1556vw(sh)	1543w(sh)	
1534vvs	1533mw	1529vvs	1534m	1530vvs	1526ms	ν(C=O)
				1522vvs		
1507s(sh)	1505m	1504m(sh)	1504m	1498ms(sh)	1504mw	ν(C—C)m
1490ms	1489vw(sh)	1489mw	1492vs(sh)	1488mw(sh)		
1464vs	1465m	1463m	1466mw	1462ms	1465mw	ν(C—C)n
1422vs	1441ms	1438ms	1441ms	1441s	1440s	ν(C=N(
				1435s		
1424m(sh)		1422w	1423vw(sh)		1423vw(sh)	δ_a(C—H)
		1418w	1416vvw(sh)	1418mw		
1402w(sh)	1402vvw	1397vvw(br)		1398vw(sh)		Combin. (u + v)
1334vvw(br)		1358vvw(br)	1363vvw(br)			
1318w	1319vvw	1316vvw	1320vvw	1316vvw	1320vvw	ν(C—C)o
				1311vvw		
1296vw	1296vw(sh)	1295vvw	1294vw(sh)	1298vw	1295vw(sh)	β(C—H)a
				1289vvw		

1280vw	1282mw(sh)	1280vvw(br)	1281m		1280m	X-sens. q
1250vvw(br)			1258vw(sh)		1249vvw(br)	
				1243vvw		
1197vw	1199w	1196vw	1198w	1196vw	1196w	δ_s(C—H)
1193vvw(sh)		1190vvw(sh)				Combin. (u + v)
1183vvw(sh)	1183vvw	1183vvw(sh)		1186vvw	1185vw(sh)	
1174vw	1174vvw	1173vvw		1174vvw	1179vw(sh)	β(C—H)a
1161mw	1162vw(sh)	1160w	1161w	1162vw	1158w	β(C—H)c
1154mw	1155w	1152w	1156w	1153mw	1152w	
1112vvw		1109vvw(br)		1111vvw(br)		Combin.
1096vvw		1094vvw(br)		1095vvw(br)		Combin.
1079w		1078vw		1081w	1083vvw	β(C—H)d
					1076vvw	
1040m	1040vvw(sh)	1038mw		1040mw	1034vvw(br)	
1016ms	1020vw	1014mw	1023vvw(br)	1018m	1019vw(sh)	β(C—H)b
1000vw	1004vs	1000vw	1004vs	1003vw	1006vvs	Ring p
990vvw	990vvw(sh)			992vvw(sh)		γ(C—H)j
975vvw		974vvw		979vvw	980vvw	γ(C—H)h
				944vw(sh)		
939s		937ms	930vvw	940ms	938vvw	
928ms		930m		932ms		ν(N—O)
		927m		920w(sh)		
890vvw					894vvw	γ(C—H)i
855vvw(br)	844vw	852vvw(br)	843w	854vvw(br)	837vvw	γ(C—H)g
		803vw(sh)	794vvw(sh)	806vw(sh)		
781s	782vw	780ms	784vw	781s	781vw	X-sens. r
770vs		774ms		775s	770vvw(sh)	
		769ms		769s		
723s	724vw	722m	724vw	723ms	722vw	γ(C—H)f
	705vvw	705m	707vvw	705s	705vvw	
701s		701m		701s		
691s	690vvw	693m	693vvw	693ms	690vvw	ϕ(C—C)v
		623vw	624w(sh)			
619vw(sh)	618w	619vw(sh)	619w	620vw	618w	α(C—C—C)s
569ms	570w	569mw		572mw	570vw	$\}\nu_a$(Sn—C)
	566w		564w	560vvw	557vw	
535vw	532s	531vvw	532vs	528vw	528vvs	$\}\nu_s$(Sn—C)
		528vvw			523vs	
512vw	512vw	511vw	513w	512vw		X-sens. t
484vw	485vvw	484vvw	484vvw	484vw	483vvw	X-sens. y
	481vvw		472vvw			
449w(sh)		443vw(sh)	440vvw	443w(sh)		ν_a(Sn—O)
440mw		437w		439mw		

TABLE 17 (Continued)

$(CH_3)_2Sn(Cl)[ON(Ph)COPh]$		$(CH_3)_2Sn(Br)[ON(Ph)COPh]$		$(CH_3)_2Sn(I)[ON(Ph)COPh]$		Assignments
IR [a]	Raman [b]	IR [a]	Raman [b]	IR [a]	Raman [b]	
412vw(sh)	412vw		413w		410w	ν_s(Sn—O)
406w	407vw(sh)	406vw	406vw(sh)	406vw	407w	ϕ(C—C)w
401vw(sh)		4400vvw(sh)		401vvw(sh)		
360vw		360vw	362vvw	363vvw		
303mw(sh)	302vw(sh)					
293m	291w					ν(Sn—Cl)
	282vw(sh)					
	251w		253w		251w	X-sens, u
	223vw		225w		224vw	
	209vvw		208w		211vvw	ν(Sn—Br) + ligand
	180vvw		182vw		187vw	
					159s	
					153s	ν(Sn—I)
					140	
					114	
					104	

[a] Recorded as nujol and halocarbon mulls. [b] Compacted Powder.

amines follow the predicted pattern in that the more electronegative the halogen, then the greater the redistribution of electron density, and thus the larger distortion leading to a greater value of $^2J(^{119}Sn—C—^1H)$.

Structures of the type XXVI suggested by the Mössbauer and PMR spectra, are expected to exhibit two tin—carbon stretching modes and one tin—halogen stretching mode, which should all be both Raman and infrared active. The assignment of the symmetric tin—carbon stretch to a band at ca. 530 cm^{-1}, apparent in the spectra of all three compounds, occurring as an intense absorption in the Raman, and as a fairly weak band in the infrared. The symmetric tin—carbon stretch of the iodo compound is split in the Raman. The antisymmetric tin—carbon stretching frequency is also readily assigned to the bands occurring comparatively strongly in the infrared at ca. 570 cm^{-1}, mirrored in the Raman by weak bands, although the spectra of the iodo compound also show duplication of this vibration. This duplication is also a feature of the tin—iodine stretching vibration which can clearly be assigned to the two Raman intense bands at 159 and 153 cm^{-1}, on the basis of their intensity and lack of comparable absorptions in the Raman spectra of the other derivatives. The tin—chlorine stretching mode, can be expected to occur at ca. 300 cm^{-1} in this instance. However, this region exhibits three absorptions in the spectra of the bromo and iodo compounds. The comparatively weak shoulder at 282 cm^{-1} appears only in the Raman, and since this mode is expected to be both infrared and Raman active, it can be discounted. The band at 303 cm^{-1} occurs as a shoulder, in both Raman and infrared, to the more intense absorption at 293 cm^{-1}, which is assigned the Sn—Cl stretching mode. On initial inspection, the tin—bromine stretching vibration is not obvious, as the absorptions below 250 cm^{-1} in the Raman spectrum of $(CH_3)_2Sn(Br)[ON(Ph)COPh]$ are common to the spectra of both the chloro and iodo compounds. However, the significantly increased intensity of the band at 208 cm^{-1}, in comparison with the corresponding extremely weak absorptions in the other two compounds, suggests that this be tentatively assigned to the Sn—Br stretching mode.

The duplication of tin-substituent stretching modes and of the carbonyl stretching frequency in the iodo compound strongly suggest the existence of two crystallographically independent molecules in the unit cell, a phenomenon which occurs for $(CH_3)_3Sn[ON(Ph)COPh]$ [6].

The mass spectra of $(CH_3)_2Sn(Cl)[ON(Ph)COPh]$ (Table 18) and $(CH_3)_2Sn(Br)[ON(Ph)COPh]$ (Table 19) were recorded by direct insertion into the ion chamber at 160 and 170°C respectively, as a result of their comparative involatility. Both spectra exhibit stepwise fragmentation through loss of the major substituents. Chelate ring contractions through loss of oxygen, are not as evident as they have been with some of the other hydroxylamine derivatives, giving only a weak fragment, at *m/e* 330 in the spectrum of the chloro derivative, and two fragments at *m/e* 409 and 394 in the bromo derivative. However, ring contractions through loss of the nitrene species [:NPh] appear more favourable, giving ions of significant intensity in both spectra; at *m/e* 290, 270 and 240, for the chloro compound, and at *m/e* 270 and 240 for the bromo compound. A little surprisingly the base peaks of both spectra are dihalogenotin containing fragments occur in both spectra which are at *m/e* 525 and 219 in the chloro compound, the latter of which is assigned to the $(CH_3)_2SnCl_2^+$ ion, and at *m/e*

TABLE 18

THE MAJOR FRAGMENTS IN THE MASS SPECTRUM OF $(CH_3)_2Sn(Cl)[ON(Ph)COPh]$ [a,b]

m/e	Relative intensity [c]	Assignment
425	1.63	
396	2.38	$(CH_3)_2Sn(Cl)[ON(Ph)COPh]^+$
381	80.00	$(CH_3)Sn(Cl)[ON(Ph)COPh]^+$
361	25.00	$(CH_3)_2Sn[ON(Ph)COPh]^+$
350	1.75	
331	[d]	$Sn[ON(Ph)COPh]^+$
330	[d]	$(CH_3)Sn[N(Ph)COPh]^+$
313	1.63	
292	[d]	
290	5.75	$(CH_3)Sn(Cl)[O_2CPh]^+$
270	20.00	$(CH_3)_2Sn[O_2CPh]^+$
249	20.00	
240	7.50	$Sn[O_2CPh]^+$
226	4.26	$Sn[ONPh]^+$
219	8.63	$(CH_3)_2Sn(Cl)_2^+$
204	100.00	$(CH_3)Sn(Cl)_2^+$
197	100.00	$HN(Ph)COPh^+$
184	60.00	$(CH_3)_2Sn(Cl)^+$
169	10.62	$(CH_3)Sn(Cl)^+$
154	75.20	$Sn(Cl)^+$
134	22.50	$(CH_3)Sn^+$
119	25.10	Sn^+
106	47.30	$PhCOH^+$
105	58.20	$PhCO^+$
93	15.00	$PhNH_2^+$
92	11.26	$PhNH^+$
91	75.00	PhN^+
77	225.00	Ph^+

[a] Based on ^{119}Sn and ^{35}Cl. [b] Direct insertion at 160°C. [c] Relative to the most intense tin containing fragment. [d] Intensity obscured by overlap.

543 and 307 in the bromo analogue, and again the latter is assigned to the $(CH_3)_2SnBr_2^+$ ion. In addition, the spectrum of the bromo derivative shows several other weak peaks with tin-plus-bromine isotopic distributions at mass numbers in excess of parent. It can only be assumed, since both derivatives were carefully recrystallised, that under the influence of the high temperatures utilised, labile fragmentation leads to facile reassociation to form some more volatile components, such as the dimethyltin dihalides. An alternative interpretation is that the compounds are initially associated through halogen bridges in the solid state, although this is unlikely in light of the Mössbauer spectra, and in the absence of rational assignments in the mass in excess of parent region.

C. The rearrangements of the triorganotin hydroxylamines

The rearrangement of some of the trioganotin hydroxylamine derivatives to give tetraorganotins and diorganotin bis-hydroxylamines, has been summarily described above, and was shown to involve migration of one of the tin-bonded organo groups, rather than the (1,3) migration of the hydroxylamine substituents. *N*-Benzoyl-*N*-phenylhydroxylamine readily forms stable triorganotin derivatives,

TABLE 19

THE MAJOR FRAGMENTS IN THE MASS SPECTRA OF $(CH_3)_2Sn(Br)[ON(Ph)COPh]$ [a,b]

m/e	Relative intensity [c]	Assignment
560	0.88	
543	0.18	
467	1.41	
440	1.18	$(CH_3)_2Sn(Br)[ON(Ph)COPh]^+$
425	52.35	$(CH_3)Sn(Br)[ON(Ph)COPh]^+$
410	*d*	$Sn(Br)[ON(Ph)COPh]^+$
409	4.59	$(CH_3)Sn(Br)[N(Ph)COPh]^+$
394	0.77	$Sn(Br)[N(Ph)COPh]^+$
381	4.18	
361	39.40	$(CH_3)_2Sn[ON(Ph)COPh]^+$
331	27.08	$Sn[ON(Ph)COPh]^+$
307	15.29	$(CH_3)_2Sn(Br)_2^+$
292	100.00	$(CH_3)Sn(Br)_2^+$
277	5.88	$Sn(Br)_2^+$
270	17.65	$(CH_3)_2Sn[O_2CPh]^+$
248	13.53	
240	11.76	$Sn[O_2CPh]^+$
228	37.64	$(CH_3)_2Sn(Br)^+$
213	*d*	$(CH_3)Sn(Br)^+$
212	*d*	$(CH_2)Sn(Br)^+$
198	71.80	$Sn(Br)^+$
184	8.24	
180	38.80	$(Ph)NC(Ph)^+$
166	8.24	$(CH_3)SnO_2^+$
154	7.64	
134	43.55	$(CH_3)Sn^+$
133	*d*	$(CH_2)Sn^+$
132	*d*	$(CH)Sn^+$
119	37.64	Sn^+
106	117.60	$PhCOH^+$
105	824.00	$PhCO^+$
93	76.50	$PhNH_2^+$
91	193.80	PhN^+
78	95.40	$Ph—H^+$
77	*e*	Ph^+

[a] Based on ^{119}Sn and ^{79}Br. [b] Direct insertion at 170°C. [c] Relative to most intense tin-containing fragment. [d] Intensities weak and obscured by overlap. [e] Intensity off scale.

whilst the analogous *N*-acetyl-*N*-methylhydroxylamine only forms the trimethyltin derivative under extremely mild conditions, giving the corresponding dimethyltin derivative under the comparatively mild thermal conditions of refluxing diethyl ether. Similarly the hydroxamic acids, *N*-acetylhydroxylamine and *N*-benzoylhydroxylamine gave $(CH_3)_2Sn[ON(H)COCH_3]_2$ and Ph_4Sn respectively when refluxed with $(CH_3)_3SnOH$ and Ph_3SnOH in benzene. However $(CH_3)_3Sn[ON(H)COPh]$ and $(n\text{-}C_3H_7)_3Sn[ON(H)COPh]$ were obtained under similar conditions, and the triphenyltin *N*-benzohydroximate anion was obtained from the reaction of Ph_3SnCl, $HON(H)COPh$ and excess $N(C_2H_5)_3$ in methanol at ambient temperature. When the latter reaction was repeated with a stoichiometric quantity of $N(C_2H_5)_3$ in refluxing methanol, Ph_4Sn was obtained.

The crystal structure of $(CH_3)_3Sn[ON(Ph)COPh]$ [6] and $Ph_3Sn[ON$-

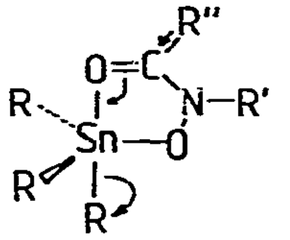
(Ph)COPh] [2] show the molecules to contain five-coordinated tin with the axially-bonded organic group at a significantly longer Sn—C distance than the two equatorially bonded groups. Since the axial organic group is mutually *trans* to the intramolecularly coordinating carbonyl oxygen atom, it is reasonable to assume that the rearrangements take place via the migration of the axially-bound organic, with nucleophilic assistance of the carbonyl group.

The substituents of the hydroxylamine residue obviously influence the rearrangement, since the *N*-benzoylhydroxylamine derivatives rearrange more readily than the corresponding *N*-benzoyl-*N*-phenylhydroxylamine derivatives, and whereas $(CH_3)_3Sn[ON(H)COPh]$ was obtained as a stable product, under identical conditions the analogous $(CH_3)_3Sn[ON(H)COCH_3]$ compound appears to rearrange giving $(CH_3)_2Sn[ON(H)COCH_3]_2$ as the only isolated product.

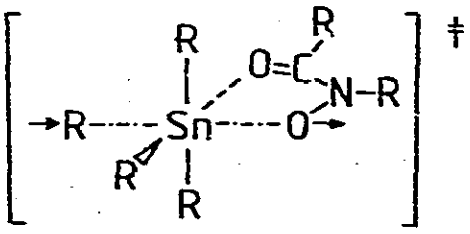
The nature of the tin-bonded organic group also appears to influence the rearrangement, since the hydroxamate derivative $(CH_3)_3Sn[ON(H)COPh]$ is readily formed in boiling benzene, whereas under the same conditions tetraphenyltin is the only identifiable product in the attempted preparation of $Ph_3Sn[ON(H)COPh]$.

The rearrangements take place in both protic and aprotic solvents, and are clearly facilitated by heat. The compound $(CH_3)_3Sn[ON(CH_3)COCH_3]$ was stable in chloroform for several months at ambient temperature, yet was observed to rearrange to $(CH_3)_2Sn[ON(H)COCH_3]_2$ in refluxing ether, and decomposed at ca. 70°C in the solid state.

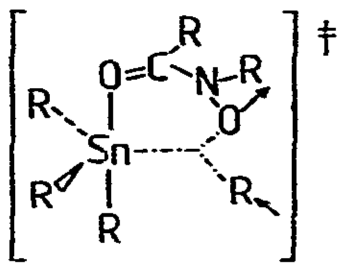
The most probable mechanism, therefore, involves the formation of an alkyl carbanion by cleavage of the axially bonded R group XXVII. Such a mechanism would be facilitated by electron donating R″ groups (CH_3 more facilitating than Ph groups), and electron accepting R groups (Ph more facilitating than CH_3 groups), as observed. The carbanion is then capable of nucleophilic attack on a further $R_3Sn[ON(R')COR'']$ species, either by inversion of the pyramidal R_3Sn moiety, forming a six-coordinate transition state XXVIII or by displacement of an oxygen atom of the hydroxylamine group to form an essentially five-coordinate transition state XXIX. Both transition states will be encouraged to rearrange to the R_4Sn species by cleavage of the covalent tin—oxygen bond by electron with drawing nitrogen substituents or, by the loss of the labile nitrogen bonded proton of the hydroxamates. The hydroxylamine anion is then free to



(XXVII)



(XXVIII)



(XXIX)

condense with the diorganotinhydroxylamine cation to form $R_2Sn[ON(R')COR'']_2$. Although the mechanism is presented in a stepwise fashion, the reaction is equally likely to proceed via a complex bimolecular cyclic transition state. However in the absence of kinetic data the nature of the transition state must be regarded as surmise.

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