of Grummit, Budewitz, and Chudd.[33] To 6.0 g (260 mg-atom) of magnesium powder (40 mesh) in *ca.* 125 ml of ether, freshly distilled from lithium aluminum hydride, in a flame-dried 300-ml round-bottomed flask equipped with magnetic stirrer, condenser, and No-Air stopper, was added at 0° *ca.* 0.5 ml of 1,2-dibromoethane. To the activated magnesium, 7.0 g (58 mmol) of freshly distilled allyl bromide was added at 0° over a 2-hr period. The solution was allowed to stir at 0° for an additional 5 hr and was transferred by cannula to a flame-dried 200-ml storage bottle. The residual salts were washed with *ca.* 20 ml of ether, and the washings transferred to the storage bottle and mixed thoroughly. Titration with 0.105 *M sec*-butyl alcohol in xylene using 1,10-phenanthroline[34] as indicator showed the solution to be 0.36 *M*.

Tetra(*trihapto*allyl)zirconium(IV) (5) was prepared according to the procedure of Becconsall, Job, and O'Brien.[7] In a 100-ml round-bottomed flask was placed 0.79 g (3.9 mmol) of zirconium tetrachloride. To the salt, cooled to −60°, 40 ml of 0.30 *M* (12.0 mmol) allylmagnesium bromide was added over a 1.5 hr period. The mixture was stirred for 20 hr at external temperature of *ca.* −70° (Dry Ice–isopropyl alcohol) and filtered at *ca.* −40° through a Celite pad, which previously had been dried with *ca.* 2 ml of *n*-butyllithium. The solvent was removed under vacuum while maintaining the sample temperature between −40 and −30°.

Preparation of Nmr Samples of 5. *Ca.* 5 ml of fluorotrichloromethane, previously degassed by three freeze–thaw cycles, was distilled into the storage tube containing the red solid **5**, obtained by removal of ether under vacuum at −78° (Dry Ice–isopropyl alcohol). An aliquot of the resulting solution was transferred at −78° through a stainless steel cannula into an nmr tube, adapted with a 12/15 ball joint and joined to a vacuum stopcock, fitted with a No-Air stopper. TMS internal standard was added and the tube sealed under vacuum. The sample used showed no absorption in the nmr spectrum due to ether, but did show a broad impurity peak centered slightly upfield from the H_1 resonances of **5**. The nature of this impurity was not explored. Extensive decomposition was observed if the sample was not stored below −20°.

***Trihapto*allylpalladium chloride dimer** was prepared by Dr. D. L. Tibbets. The nmr sample used in this study was prepared by adding 75 mg (0.206 mmol) of the palladium complex and 64.5 mg (0.826 mmol) of dimethyl sulfoxide-d_6 (2 equiv of DMSO-d_6/allyl group) to 0.5 ml of a 10% solution of benzene in deuteriochloroform.

Calculations were performed at the Massachusetts Institute of Technology Information Processing Center using the program EXCHSYS[15,35] to compute eigenfunctions and line shapes of static spectra, K matrices, and interchange-broadened line shapes.

Registry No. Tetra(*trihapto*allyl)zirconium(IV), 12090-34-5; chloro(*trihapto*allyl)palladium(II) dimer, 12012-95-2.

Acknowledgment. The cooperation of D. L. Tibbets in obtaining the nmr spectra is appreciated. C. B. Powell, Jr., and J. B. Lisle assisted with the computer programming. Our colleague John Waugh corrected a number of our egregious misconceptions concerning the physical basis of magnetic resonance phenomena.

(33) O. Grummit, E. P. Budewitz, and C. C. Chudd, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 748.

(34) S. C. Watson and J. F. Eastham, *J. Organometal. Chem.*, 9, 165 (1967).

(35) EXCHSYS is based on the program LAOCN3: A. A. Bothner-By and S. M. Castellano, in D. F. deTar, "Computer Programs for Chemistry," Vol. I, W. A. Benjamin, New York, N. Y., 1968, and local line shape programs, KMATRX and EXCNMR, written by J. B. Lisle, C. P. Powell, J. K. Krieger, and G. M. Whitesides.

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Structural Studies in Main-Group Chemistry. IV.[1] *O*-Trialkyltin Hydroxylamines[2]

PHILIP G. HARRISON

Received November 15, 1972

The organotin hydroxylamine derivatives $Me_3SnONEt_2$, $R_3SnONHCOPh$ (R = Me, *n*-Pr), and $R_3SnONPhCOPh$ (R = Me, *n*-Pr, Ph) and the organosilicon and organolead analogs $Me_3SiONPhCOPh$ and $Ph_3PbONPhCOPh$ have been synthesized. All are inert to hydrolysis save $Me_3SnONEt_2$, which readily reverts to its protic precursors in air, and monomeric in solution (osmometry). Attempts to prepare $Ph_3SnONHCOPh$ from triphenyltin hydroxide result in the formation of tetraphenyltin in high yield, and from triphenyltin chloride and excess triethylamine the ionic species $(NEt_3H^+)(Ph_3\overline{SnONCPhO}^-$ is produced. The trimethyltin homolog of the latter is prepared by dissolution of $Me_3SnONHCOPh$ in triethylamine. The structures of the derivatives in both solution and solid phases are discussed in terms of their infrared, nuclear magnetic resonance, tin-119m Mossbauer, and mass spectra. The stability of the tin and lead derivatives is due to the increase of the coordination number at the metal atom *via intra*molecular coordination of the carbonyl group to the metal. The mass spectra for $Me_3SnONHCOPh$ and $Me_3SnONPhCOPh$ indicate the presence of associated, most probably weakly associated dimer, species in the solid. High-resolution mass measurements have confirmed the presence of the SnOSn backbone in the more abundant ditin fragments and also the composition of monotin fragments, among which are some which arise from novel ring contraction reactions involving the elimination of oxygen or phenylnitrene from $\overline{MONPhCPh{=}O}$ heterocyclic species. The major fragmentation processes of $Me_3SiONPhCOPh$ have been corroborated by the observation of metastable ions and involve mainly the formation of phenyl-containing ions in which the charge may be effectively delocalized.

Introduction

The synthesis and properties of main-group metal and metalloid derivatives containing the M-O-N linkage continues to arouse much interest.[3,4] Oxime derivatives of lithium,[3] silicon, germanium, tin,[3,4] lead, arsenic, and antimony[4] have previously been synthesized by us, while attempts to prepare similar phosphorus derivatives led to the formation of phosphorylamines *via* an Arbuzov rearrangement.[4] The *O*-(trialkylstannyl)oximes[3] are volatile monomeric liquids except for cyclohexanone *O*-(trimethylstannyl)oxime, for which infrared, tin-119m Mossbauer, and high-resolution mass spectral data indicated association *via* distannoxane $\overline{SnOSnO}$ ring formation in the solid. Such association is however rather weak since only monomeric species could be

(1) Part III: P. G. Harrison and J. J. Zuckerman, *J. Organometal. Chem.*, in press.

(2) A preliminary communication has appeared: P. G. Harrison, *J. Organometal. Chem.*, 38, C5 (1972).

(3) P. G. Harrison and J. J. Zuckerman, *Inorg. Chem.*, 9, 175 (1970), and references therein.

(4) P. J. Harrison and J. J. Zuckerman, *Inorg. Nucl. Chem. Lett.*, 6, 5 (1970), and references therein.

detected in benzene solution, unlike the strongly associated 1,3-disubstituted distannoxanes where dimeric units are preserved on dissolution.(5) Because of their different electronic and steric requirements, we have found it of interest to synthesize organotin derivatives of substituted hydroxylamines, some initial investigations of which are reported in this paper.

Results and Discussion

The organotin derivatives of *N*,*N*-diethyl-, *N*-benzoyl-, and *N*-phenyl-*N*-benzoylhydroxylamines were prepared by the azeotropic removal of water from the appropriate hydroxylamine and the organotin oxide or hydroxide

$$\begin{matrix} {}^1\!/_2(R_3Sn)_2O \\ \text{or} \\ R_3SnOH \end{matrix} + HONR^1R^2 \xrightarrow{-H_2O} R_3SnONR^1R^2 \qquad (1)$$

Ia, R = Me, R^1 and R^2 = Et
b, R = Me, R^1 = H, R_2 = COPh
c, R = *n*-Pr, R^1 = H, R^2 = COPh
d, R = Me, R^1 = Ph, R^2 = COPh
e, R = *n*-Pr, R^1 = Ph, R^2 = COPh
f, R = Ph, R^1 = Ph, R^2 = COPh

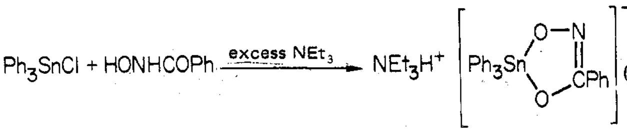
O-(Triphenyllead)-*N*-phenyl-*N*-benzoylhydroxylamine (II) was similarly synthesized from triphenyllead hydroxide

$$Ph_3PbOH + HONPhCOPh \xrightarrow{-H_2O} \underset{\text{II}}{Ph_3PbONPhCOPh} \qquad (2)$$

However attempts to prepare $Ph_3SnONHCOPh$ by the same method only resulted in the formation of tetraphenyltin in high yield, presumably by a disproportionation reaction, although no pure diphenyltin derivative could be isolated

$$Ph_3SnOH + HONHCOPh \xrightarrow{-H_2O} [Ph_3SnONHCOPh] \longrightarrow Ph_4Sn + [Ph_2Sn(ONHCOPh)_2] \qquad (3)$$

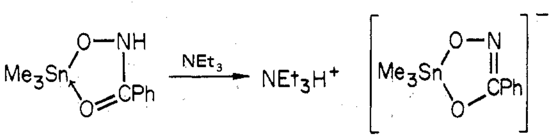
The reaction of the hydroxylamine with triphenyltin chloride in the presence of triethylamine yielded a product, the triethylammonium salt of the tin-containing complex anion, IIIa, only when a large excess of amine was used



(4)

IIIa

Dissolution of $Me_3SnONHCOPh$ in triethylamine yielded the trimethyltin homolog, IIIb



(5)

IIIb

Since the Lewis acidity of the trimethylsilyl moiety is much lower than that of the heavier group IV metals, the *O*-trimethylsilyl derivative of *N*-phenyl-*N*-benzoylhydroxylamine (IV) was synthesized for comparative purposes. Because of the inertness of the silicon-oxygen bonds of hexamethyldisiloxane, this compound was synthesized by the protolysis of the silicon-nitrogen bonds of the analogous disilazane

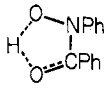
$${}^1\!/_2(Me_3Si)_2NH + HONPhCOPh \xrightarrow{-NH_3} \underset{\text{IV}}{Me_3SiONPhCOPh} \qquad (6)$$

Like *O*-(trimethylstannyl)acetoxime,(3) the *O*-trimethyltin derivative of *N*,*N*-diethylhydroxylamine is a mobile liquid, which hydrolyzes readily in air to its component protic reagents, characteristic of the tin-oxygen bonds of four-coordinate tin compounds. The feature of highest mass in the mass spectrum (Table I) is the polyisotopic parent ion at *m*/*e* 252. Other monotin-containing fragments produced by the fission of tin-carbon and tin-oxygen bonds are observed at lower mass. Corroboration of the unassociated nature of the compound comes from the nmr ${}^2J({}^{117,119}Sn\text{-}C\text{-}{}^1H)$ coupling constant, which appears to be sensitive to the coordination number at tin for methyltin derivatives. The value of this parameter for the trimethyltin derivatives of *N*,*N*-diethylhydroxylamine, acetoxime,(3) and cyclohexanone oxime(3) all lie close to that for tetramethyltin (∿54 Hz) which is unable to associate.

The organotin derivatives of the *N*-benzoylhydroxylamines are, in contrast, extremely stable to moisture. Colligative measurements (osmometry) show that the derivatives of *N*-phenyl-*N*-benzoylhydroxylamine are monomeric in dilute chloroform solution. Similar measurements for *O*-(trimethylstannyl)-*N*-benzoylhydroxylamine indicated some association. Evidence for association *via* hydrogen bonding of the nitrogenous proton comes from infrared dilution studies on the latter compound and its tripropyltin analog. The neat compounds exhibit a very broad N-H stretching frequency at *ca.* 3200 cm^{-1}. On dissolution in dichloromethane, a second band of much narrower line width appears to higher energy at *ca.* 3410-3430 cm^{-1}, until, at concentrations of $\lesssim 1\%$, only the higher frequency band remains.

Information concerning the colligative nature in the solid phase is available from the mass spectra of $Me_3SnONHCOPh$, $Me_3SnONPhCOPh$, and $Ph_3SnONPhCOPh$, for which relevant data are listed in Tables II-IV, respectively. In addition to monotin-containing fragments derived from fission of the monomer units, all three compounds exhibit several ditin-containing fragments. Furthermore, in the spectra of the two trimethyltin derivatives, there occur monotin fragments of mass in excess of the monomer parent ion. In contrast, the spectra of the *O*-trimethylsilyl (Table V) and *O*-triphenyllead (Table VI) compounds show only ions resulting from the fragmentation of a monomer species.

Recently we have completed a determination of the crystal structure of $Ph_3SnONPhCOPh$.(6) The compound possesses a trigonal-bipyramidal arrangement of groups about tin, with two equatorial and one axial phenyl groups (Figure 1). The hydroxylamine residue is covalently bound at an equatorial site, and the carbonyl group coordinates *intra*molecularly to the tin atom *via* the remaining axial site. This is consistent with the lowering of the infrared carbonyl stretching frequency from 1620 cm^{-1} in the parent hydroxylamine to 1540 cm^{-1} in the *O*-triphenyltin derivative. Similar shifts to lower energy for this mode are observed for the other tin and lead derivatives of the *N*-benzoylhydroxylamines in both the solid and solution. In the *O*-trimethylsilyl derivative, however, a shift to *higher* energy (1660 cm^{-1}) is observed. This value is perhaps more truely representative of a "free," uncoordinated carbonyl group in this type of compound, since *inter*- or *intra*molecular hydrogen bonding of the type



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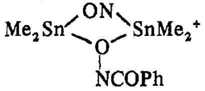
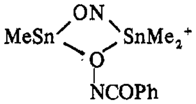
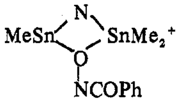
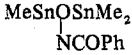
(5) R. Okawara and M. Wada, *Advan. Organometal. Chem.*, 5, 151 (1967).

(6) T. J. King and P. G. Harrison, *J. Chem. Soc., Chem. Commun.*, 815 (1972).

Table I. Mass Spectral Data for the Tin-Containing Fragments of $Me_3SnONEt_2$

Mass	Rel intens	Assignment
252	17.6	$Me_3SnONEt_2^+$
237	11.0	$Me_2SnONEt_2^+$
207	3.5	$SnONEt_2^+$
184	8.3	$C_5H_5Sn^+$?
164	100	Me_3Sn^+
149	9.7	Me_2Sn^+
134	16.9	$MeSn^+$
119	4.9	Sn^+

Table II. Mass Spectra Data for the Mono- and Ditin Fragments of $Me_3SnONHCOPh$

Mass	Rel intens	Assignment
	Ditin Fragments	
570	1.1	$[Me_2SnONHCOPh]_2^+$
463	0.3	
448	28.6	
432	0.8	
418	0.7	 $\mathrm{MeSn}\underset{\mathrm{NCOPh}}{\mathrm{O}}\mathrm{SnMe_2^+}$
329[a]	100	$Me_3SnOSnMe_2^+$
313	5.2	$Me_3Sn_2ON^+$
299	30.9	$Me_2SnOSnMe^+$
	Monotin Fragments	
361	20.5	$Sn(O_2CPh)_2^+$
345	1.2	$Sn(O_2CPh)(OCPh)^+$
285[b]	35.6	$Me_2SnONHCOPh^+$
270	14.4	$MeSnONHCOPh^+$ $Me_2SnO_2CPh^+$
255	1.2	$SnONHCOPh^+$
240	3.7	SnO_2CPh^+
226	15.1	Me_2PhSn^+
164	100	Me_3Sn^+
149	40.9	Me_2Sn^+
134	78.8	$MeSn^+$

[a] Mass measurement: Found: 329.9242. Calcd: Me_5Sn_2O, 329.9179; $Me_3Sn_2O_2N$, 329.8689. [b] Mass measurement: Found: 285.9837. Calcd: 285.9869.

Table III. Mass Spectral Data for the Mono- and Ditin Fragments for $Me_3SnONPhCOPh$

Mass	Rel intens	Assignment
	Ditin Fragments	
737	1.6	$[\text{dimer}-Me]^+$
543	9.6	$[\text{dimer}-(Me + Ph + C_2O)]^+$
527	4.4	$Me_5Sn_2O_2N_2Ph_2^+$
450	3.4	$Me_5Sn_2O_2N_2Ph^+$
436	3.2	$Me_5Sn_2O_2NPh^+$
391	13.0	$Me_3Sn_2O_2NPh^+$
329[a]	*i*	$Me_3SnOSnMe_2^+$
299	100	$Me_2SnOSnMe^+$
	Monotin Fragments	
559	0.4	*j*
467	0.2	*j*
423	0.8	*j*
407	0.4	*j*
376	1.7	$Me_3SnONPhCOPh^+$
361	100	$Me_2SnONPhCOPh^+$
345[b]	17.2	$Me_2SnOCPhNPh^+$
331[c]	20.0	$SnONPhCOPh^+$
313[d]	6.1	$SnN{=}C{=}NPh_2^+$
287[e]	8.3	$Me_2SnO_2N_2HPh^+$
270[f]	17.2	$Me_2SnO_2CPh^+$
240[g]	23.5	SnO_2CPh^+
226[h]	36.1	Me_2PhSn^+
164	83.4	Me_3Sn^+
149	8.9	Me_2Sn^+
134	36.1	$MeSn^+$

[a-h] The following footnotes contain found and calculated high-resolution mass measurements, respectively. [a] 329.9203, 329.9179. [b] 346.0219, 346.0253. [c] 329.9736, 329.9729. [d] 314.0757, 314.0419. [e] 287.9859, 287.9920. [f] 270.9779, 270.9780. [g] 240.9356, 240.9311. [h] 226.9884, 226.9882. [i] Intensity measurement not possible because of overlapping monotin and ditin fragments. [j] Not assigned.

Table IV. Mass Spectral Data for Mono- and Ditin Fragments for $Ph_3SnONPhCOPh$

Mass	Rel intens	Assignment
	Ditin Fragments	
716	16.4	$Ph_3SnOSnPh_3^+$
639	100	$Ph_3SnOSnPh_2^+$
621	7.6	*a*
562	*b*	$Ph_2SnOSnPh_2^+$
281	6.0	
	Monotin Fragments	
562	1.3	$Ph_3SnONPhCOPh^+$
546	0.9	$Ph_3SnOCPhNPh^+$
518	0.3	$Ph_3SnNPh_2^+$
485	100	$Ph_2SnONPhCOPh^+$
469	4.9	$Ph_2SnOCPhNPh^+$
426	0.7	$Ph_3Sn(c\text{-}Hex)^+$ [c]
394	10.5	$Ph_3SnO_2C^+$
350	64.4	Ph_3Sn^+
331	3.1	$SnONPhCOPh^+$
290	5.6	Ph_2SnOH^+
273	9.0	Ph_2Sn^+
240	3.5	$PhSnO_2C^+$
212	1.3	$PhSnO^+$
196	44.1	$PhSn^+$
136	6.1	$SnOH^+$
119	25.5	Sn^+

[a] Not assigned. [b] Intensity measurement not possible because of overlapping mono- and ditin fragments. [c] c-Hex = cyclohexadienyl.

is likely to occur in the parent hydroxylamine, lowering the carbonyl stretching frequency to that observed in both the solid and the chloroform solution (1620 cm^{-1}).

Since $Ph_3SnONPhCOPh$ is unequivocally monomeric in the solid phase, we attribute the observation of ditin fragments in the mass spectrum to the decomposition of the solid under electron impact at the temperature of the inlet (140°). The observed ditin fragments at *m/e* 716, 639, and 562 are all derived from $Ph_3SnOSnPh_3$, which may be a product of the thermal decomposition. Such reactions of this and related compounds are the subject of further investigation in this laboratory. In the cases of the two trimethyltin derivatives, however, no decomposition was observed at the inlet temperature used. Moreover, a greater number of fragments attributable to the fission of dimer species were observed for these compounds than for $Ph_3SnONPhCOPh$, including some indicative of the loss of only methyl groups from a dimer species.

It seems likely that, whereas $Ph_3SnONPhCOPh$ is monomeric in both the crystal and solution phases, the trimethyltin derivatives are associated in the solid. The intermolecular forces must however be fairly weak since monomeric species, which presumably also have the trigonal-bipyramidal structure, are present in solution. In the absence of additional structural information, however, it is difficult to assess

Table V. Major Fragments in the Mass Spectrum of $Me_3SiONPhCOPh$

Mass	Rel intens	Assignment
286	8.7	$(P + 1)^+$
285	33.7	$Me_3SiONPhCOPh^+$
271	13.7	$(P - Me + 1)^+$
270	33.7	$Me_2SiONPhCOPh^+$
197	8.1	
196	5.0	$PhNCOPh^+$
195	6.9	
193	10.0	$Me_2SiONPhCO^+$
180	10.0	$Me_3SiONPh^+$
167	3.8	
151	3.4	Me_2SiOPh^+
135	4.6	$SiONPh^+$
119	7.2	$PhN{=}C{=}O^+$
106	31.1	$PhCOH^+$
105	93.6	$PhCO^+$
93	6.9	PhO^+
91	16.2	PhN^+
78	14.3	$C_6H_6^+$
77	100	$C_6H_5^+$
76	8.1	$C_6H_4^+$
75	33.7	
74	3.8	Me_2SiO^+
73	24.3	
65	10.6	
59	6.9	$MeSiO^+$
51	23.1	

Table VI. Mass Spectral Data for the Lead-Containing Fragments of $Ph_3PbONPhCOPh$

Mass	Rel intens	Assignment
650	0.04	$Ph_3PbONPhCOPh^+$
573	0.11	$Ph_2PbONPhCOPh^+$
557	0.07	$Ph_2PbOCPhNPh^+$
482	3.0	$Ph_3PbO_2C^+$
438	100	Ph_3Sn^+
419	1.4	$PbONPhCOPh^+$
396	23.2	?
328	0.54	$PhPbO_2C^+$
284	72.7	$PhPb^+$
207	86.3	Pb^+

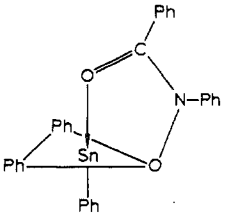
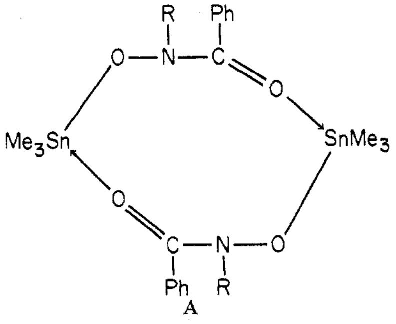
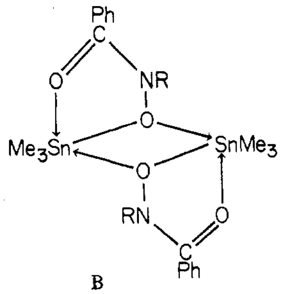


Figure 1. The structure of *O*-(triphenylstannyl)-*N*-phenyl-*N*-benzoylhydroxylamine.

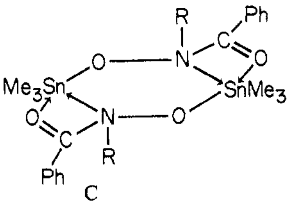
the degree of association in the solid. Dimerization, which is implied by the mass spectral data, would lead to possible formulations such as A, B, or C, while association may take place *via* the formation of linear chains, as in D, involving planar trimethyltin moieties, frequently encountered among trimethyltin derivatives in the solid state.[7] This last structure may reasonably excluded however, since for this geometry only one infrared active tin-carbon stretching frequency is expected, contrary to observation (*vide infra*).



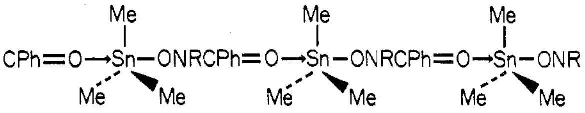
A



B



C



D

Structural information concerning the solid may also be gained from tin-119m Mossbauer spectral data, which are collected in Table VII, together with those for some related compounds. The quadrupole splittings for the model compounds $Me_3SnOSiPh_3$, $(Ph_3Sn)_2O$, and $Ph_3SnOSiPh_3$, where the bulkiness of the groups prevents any deviation from four-coordination at tin, have a value of *ca.* 2 mm/sec, close to that expected from point charge considerations of electronic imbalances in the σ framework.[8] Similarly, Me_3SnOH and trimethyl- and triphenyltin acetates, which have the five-coordinate *trans*-R_3SnX_2 structure, have quadrupole splittings $\gtrsim 3$ mm/sec. Triphenyltin oxinate, which is presumed to have the *cis*-R_3SnX_2 structure, again has a splitting of the same order as the four-coordinate R_3SnX compounds. Assignments of a four-coordinate structure to $Me_3SnONEt_2$ and the five-coordinate *cis*-R_3SnX_2 to $Ph_3SnONPhCOPh$ and the related $Ph_3SnON{=}CPhO^-$ anion are consistent with previous structural assignments made on the basis of Mossbauer data. The increased splittings for $Me_3SnONPhCOPh$ (2.36 mm/sec), $Pr_3SnONPhCOPh$ (2.65 mm/sec), and $Me_3SnONHCOPh$ (2.74 mm/sec) indicate an increasing perturbation from the *cis*-R_3SnX_2 geometry involving additional, albeit weak, coordination as in structures B or C. In $Me_3SnONHCOPh$, the association will be further reinforced by intermolecular hydrogen bonding. (See Figure 2 for a tin-119m Mossbauer spectrum of $Ph_3SnONPhCOPh$.)

Although structures A and C may not be ruled out, a structure involving dimerization *via* the formation of distannoxane rings, which are prevalent in organotin chemistry,[5] would be most likely to dissociate into monomeric species. In $Ph_3SnONPhCOPh$, the bulkiness of the phenyl rings bound to tin prevent any close *inter*molecular approach, and the smallest *inter*molecular Sn···O distances are in excess of 6.5 Å.[6] However, replacement by much smaller methyl groups would not disallow close approach for distannoxane ring formation, in which Sn-O(ring) = 2.2 Å[5] (although much longer Sn-O distances have been observed), and the formation of dimeric species would depend on the Lewis acidity of the tin atom in that particular environment. In structure B (and C) the coordination number at tin would be raised to 6, higher than

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(7) B. Y.-K. Ho and J. J. Zuckerman, *Organometal. Chem. Rev., Sect. A*, in press.

(8) R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, **4**, 65 (1970).

Table VII. Tin-119 Mossbauer Data for the Organotin Hydroxylamines and Related Compounds

Compd	IS, mm/sec	QS, mm/sec	Γ_1, mm/sec	Γ_2, mm/sec
$Me_3SnONEt_2$	1.40	1.98	1.26	1.22
$Me_3SnONPhCOPh$	1.34	2.36	1.39	1.36
$Pr_3SnONPhCOPh$	1.50	2.65	0.98	1.01
$Ph_3SnONPhCOPh$	1.26	1.94	0.92	0.92
$Me_3SnONHCOPh$	1.37	2.74	1.55	1.55
$(NEt_3H^+)(Ph_3SnONCOPh^-)$	1.23	1.74	1.81	1.88
Me_3SnOH^a	1.08	2.95		
$Me_3SnOCOMe^a$	1.34	3.47		
$Me_3SnOSiPh_3{}^a$	1.28	2.09		
$Ph_3SnOSnPh_3{}^a$	1.08	2.15		
$Ph_3SnOSiPh_3{}^a$	1.20	1.86		
$Ph_3Sn(oxinate)^a$	1.07	1.75		
$Ph_3SnOCOMe^a$	1.27	3.40		

[a] P. J. Smith, *Organometal Chem. Rev., Sect. A*, **5**, 373 (1970).

that usually accepted for coordination saturation at tin in trialkyltin compounds.

Similar coordination-dimerization equilibria in solution have been observed for 1,3-disubstituted distannoxanes[9] and the dialkyltin alkoxide halides,[10] the latter having been elegantly demonstrated by the tin-119 nmr chemical shifts of the two species present in the solution.

Although the solid-state structure of the two trimethyltin derivatives is not unequivocal, it seems certain that in solution they have the trigonal-bipyramidal structure, which will possess inequivalent tin–carbon bond distances. In $Ph_3SnONPhCOPh$ the two equatorial tin–carbon bond distances are 2.13 and 2.14 Å, while the axial distance is 2.19 Å. The proton nmr of the trimethyltin derivatives might, therefore, be expected to exhibit two distinct resonances due to the inequivalent methyl groups. One signal, together with a single set of tin-117,119 satellites, is observed in both cases. The value of ${}^2J({}^{117,119}Sn\text{-}C\text{-}{}^1H)$ of methyltin compounds, *via* a Fermi contact mechanism, is a guide to the s-electron density directed along the tin–carbon bond. We have noted before that the magnitude of this coupling constant parallels the tin–carbon bond distance, its value rising as the bond distance decreases.[11] In the compounds under discussion here, the value of ${}^2J(Sn\text{-}H)$ is ~54 Hz, a value expected for four-coordination at tin, and much lower than that observed for trans five-coordinate Me_3SnX_2 derivatives (~70 Hz). The observed proton nmr spectra are consistent with a model involving stereochemical nonrigidity of the groups about tin, the value of the coupling constant being such that one cannot distinguish between four-coordinate tetrahedral and five-coordinate cis trigonal-bipyramidal trimethyltin compounds. This may be rationalized since the latter may be regarded as rather distorted tetrahedral with smaller CSnC bond angles.

The mass spectra of the compounds merit further discussion. In the spectrum of $Me_3SnONPhCOPh$, nine ditin fragments could be distinguished. That at *m/e* 239 was shown by a high-resolution mass measurement *not* to contain nitrogen, but to possess the SnOSn backbone. The fragments of higher mass may be interpreted similarly, with organic residues pendant from the oxygen, although six-membered SnONSnON rings may not be ruled out entirely. The major fragmentation processes of the monomer involve the fission of the tin–oxygen and tin–carbon bonds, resulting in the formation of $Me_n\overline{SnOCPhNPhO}^+$ and Me_nSn^+ (n = 0–3) ions. A high-resolution mass measurement has confirmed the composition of the $\overline{SnOCPhNPhO}^+$ ion. Similar fragmentation processes were observed for the O-trimethyltin oximes, however in the present case the spectrum exhibits several monotin-containing fragments between *m/e* 226 and 345 of appreciable abundance which must arise *via* alternative fragmentation paths. The constitution of these fragments has been unequivocally determined by high-resolution mass measurements, although in the absence of metastable peaks their origin is not certain.

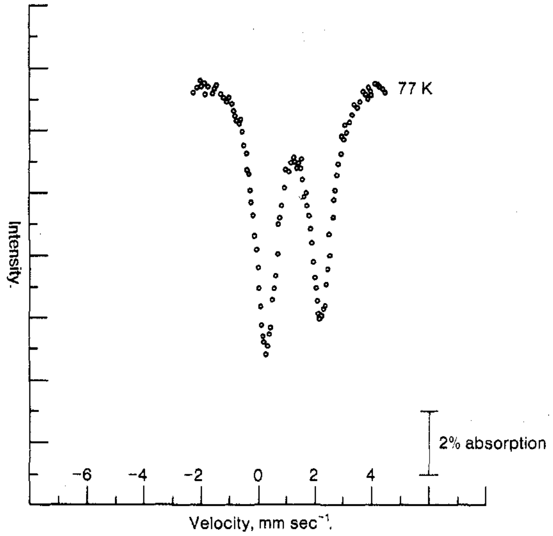
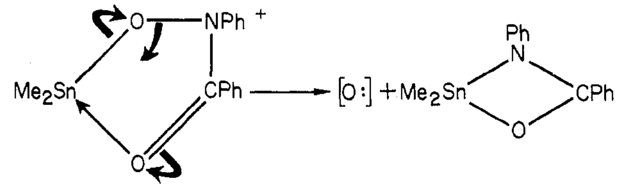


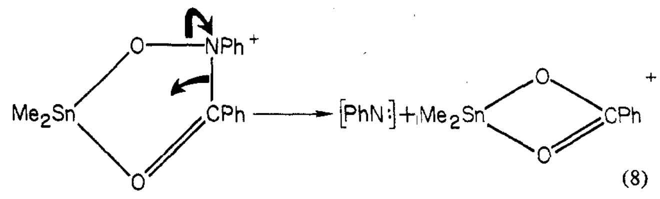
Figure 2. The tin-119m Mossbauer spectrum of $Ph_3SnONPhCOPh$ run at 77°K *vs.* a $Ba^{119m}SnO_3$ source.

The fragment of highest mass at *m/e* 345 corresponds to loss of oxygen from the $Me_2SnONPhCOPh^+$ ion. This may be readily rationalized by a ring contraction reaction involving the loss of oxygen from the tin-containing heterocyclic ring



(7)

The fragments at *m/e* 240 and 270 correspond to SnO_2CPh^+ and $Me_2SnO_2CPh^+$, respectively, and probably originate *via* a similar ring contraction reaction involving the loss of the nitrene species, PhN:



(8)

The fragment at *m/e* 226 is, surprisingly, the Me_2PhSn^+ ion. Although conceivably arising from the decomposition of the dimethyltin fragments at *m/e* 361 or 287, or by the elimination of phenyl isocyanate at *m/e* 345, its formation, necessarily *via* a 1,3-phenyl migration, is more probably by the decar-

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(9) D. L. Alleston, A. G. Davies, M. H. Hancock, and R. F. M. White, *J. Chem. Soc.*, 5469 (1963).

(10) A. C. Chapman, A. G. Davies, P. G. Harrison, and W. McFarlane, *J. Chem. Soc. C*, 821 (1970).

(11) J. Buckle, M. K. Das, and P. G. Harrison, *Inorg. Chim. Acta*, 6, 17 (1972).

Table VIII. Infrared Data (cm^{-1})[a]

Compd	ν(C=O)	ν(N–O)	ν(N–H)	ν(M–C)	ν(M–O)
HONPhCOPh	1620	922, 900			
$Me_3SiONPhCOPh$	1660	926		690 sh, 640	768
$Me_3SnONPhCOPh$	1547	935, 928		544, 524, 508	
$Pr_3SnONPhCOPh$	1557	934		610, 585 sh, 541, 500	
$Ph_3SnONPhCOPh$	1540	940			
$Ph_3PbONPhCOPh$	1543	936			
HONHCOPh	1679, 1658	897	3248 br		
$Me_3SnONHCOPh$	1567, 1543	918	3165 br	540, 520, 501	
$Pr_3SnONHCOPh$	1571, 1540	916	3200 br	600 br, 500 br	
$(NEt_3H^+)(Me_3SnONCPhO^-)$	1565, 1540, 1530	910		545, 515, 500	
$(NEt_3H^+)(Ph_3SnONCPhO^-)$	1570, 1543	918			

[a] Nujol-halocarbon oil mull or liquid film.

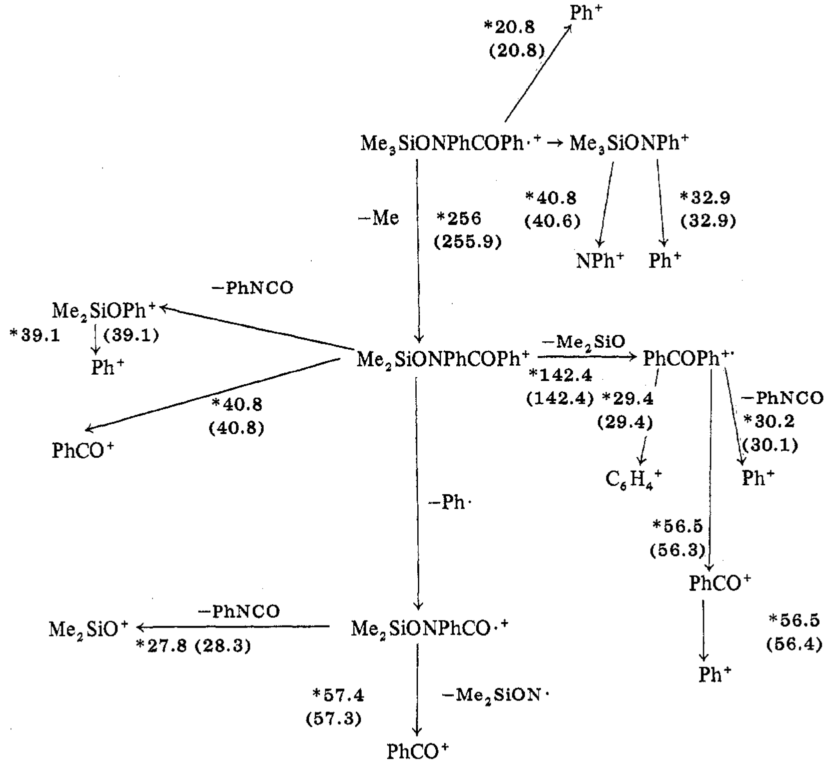

Figure 3. Major fragmentation processes of $Me_3SiONPhCOPh$. Calculated values for metastable ions are given in parentheses.

boxylation of the $Me_2SnO_2CPh^+$ ion, a process well known in main-group organometallic chemistry[12]

$$Me_2SnO_2CPh^+ \rightarrow Me_2SnPh^+ + CO_2 \qquad (9)$$

The fragment at *m/e* 287 corresponds to the $Me_2SnO_2N_2HPh^+$ ion, not the $Me_3SnO_2NPh^+$ ion, and presumably originates from the decomposition of the dimer. The mass measurement on the fragment at *m/e* 313 was not satisfactory but indicated its probable constitution as the substituted carbodiimide $Sn(Ph)N{=}C{=}NPh^+$ ion.

In general the mass spectra of $Me_3SnONHCOPh$, $Ph_3SnONPhCOPh$, and $Ph_3PbONPhCOPh$ exhibited similar fragmentation pathways, including the ring contraction reactions involving the elimination of oxygen and phenylnitrene.

Whereas the tin and lead derivatives give rise to only weak parent ions, that of the trimethylsilyl derivative IV is one of the strongest silicon-containing features of the spectrum. The major fragmentation processes, most of which have been confirmed by the observation of metastable ions, are shown in Figure 3. Cleavage of the silicon-oxygen bond is, as expected because of its high bond dissociation energy, not observed, and it is readily apparent that, on fragmentation of the hydroxylamine residue, the charge is retained by aromatic species where delocalization is possible.

Principal infrared bands for the benzoylhydroxylamines and their derivatives are listed in Table VIII. For the trimethylsilyl derivative, the silicon-oxygen and the antisymmetric and symmetric silicon-carbon stretching vibrations are located at 768, 690, and 640 cm^{-1}, respectively. The similar bands for the two trimethyltin derivatives are to be expected in the region *ca.* 500-600 cm^{-1}. In this region, both compounds exhibit three bands. For a trigonal-bipyramidal (or a distorted octahedral) structure, group theoretical considerations predict three infrared-active metal-carbon stretching frequencies; hence a total of four bands are to be expected in this region. Figure 4 shows the infrared spectra of $Me_3SnONPhCOPh$ in the region 450-600 cm^{-1} in the solid and in *ca.* 5% dichloromethane solution. The band at 508 cm^{-1} of the solid is clearly resolved into two components, at 507 and 497 cm^{-1}, on dissolution. No similar splitting could however be observed for $Me_3SnONHCOPh$. The coordinate tin-oxygen stretching vibration is extremely variable in position and is not assigned in this study. We have previously assigned this vibration for a number of phos-

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[12] G. B. Deacon, *Organometal. Chem. Rev., Sect. A*, 5, 355 (1970).

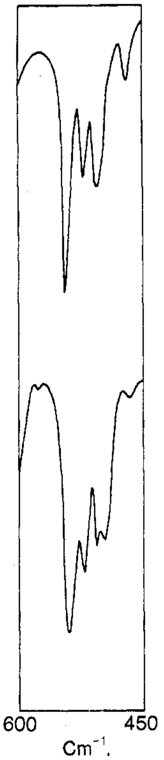

Figure 4. Infrared spectra in the region 450–600 cm^{-1} of $Me_3SnONPhCOPh$ in the solid state (upper) and in dichloromethane solution (lower).

phine and arsine oxide complexes of the stannic halides in the range 338–482 cm^{-1}.[13]

Experimental Section

All compounds with moisture-sensitive tin–oxygen and silicon–nitrogen bonds were handled under an atmosphere of dry nitrogen or argon. Infrared measurements were performed using a Perkin-Elmer 521 spectrophotometer calibrated with polystyrene film and water vapor. Mass spectra were recorded at 70 eV on an AEI MS-9 instrument. The polyisotopic tin and lead containing fragments, because of their distinctive isotope abundances,[14] are easily recognized. The *m/e* values listed in Tables I–VI are based on the isotopes tin-119 and lead-207 for convenience. Where high-resolution mass measurements have been performed, the particular isotopic peak used is self-evident. Proton nmr spectra were recorded at 100 MHz using a Varian HA-100 instrument. Osmometric molecular weight determinations were carried out in chloroform solution on a Mechrolab instrument. Tin-119m Mossbauer spectra were recorded at 77°K *vs.* a $Ba^{119m}SnO_3$ source, and the data were refined by least squares to give the best lorenztian fits.

1. **O-(Trimethylstannyl)-*N,N*-diethylhydroxylamine, Ia.** Trimethyltin hydroxide (8.0 g, 44.2 mmol) and *N,N*-diethylhydroxylamine (4.0 g, 45.0 mmol) in benzene (50 ml) were refluxed in a flask equipped with a Dean and Stark water separator. Water came over immediately and the reaction was complete within 10 min. On cooling, the solvent was removed *in vacuo* leaving the *product* as a mobile, colorless oil, bp 30–31° (0.2 mm). *Anal.* Calcd for $C_7H_{19}NOSn$: C, 33.4; H, 7.6; N, 5.6. Found: C, 33.2; H, 7.7; N, 5.4. Nmr data (CH_2Cl_2 solution): τ 9.68 (*Me*$_3$Sn), $^2J(^{117,119}Sn-^1H)$ = 55.5 Hz (unresolved); triplet τ 8.97, quartet τ 7.42 (N-*Et*), *J*(H-H) = *ca.* 7 Hz.

2. **O-(Trimethylstannyl)-*N*-phenyl-*N*-benzoylhydroxylamine, Id.** Trimethyltin hydroxide (1.81 g, 10.0 mmol) and *N*-phenyl-*N*-benzoylhydroxylamine (2.13 g, 10.0 mmol) were similarly azeotropically dehydrated. Recrystallization from cyclohexane yielded colorless needle crystals of **O-(trimethylstannyl)-*N*-phenyl-*N*-benzoylhydroxylamine**, mp 120–122°, subl pt 120° (0.1 mm). *Anal.* Calcd for $C_{16}H_{19}NO_2Sn$: C, 51.1; H, 5.1; N, 3.7 (mol wt 376). Found: C, 51.7; H, 5.1; N, 3.7 (mol wt 338 (0.022 *M*)). Nmr data (CH_2Cl_2 solution): τ 9.58 (*Me*$_3$Sn), $^2J(^{117,119}Sn-^1H)$ = 54.1, 56.7 Hz.

3. **O-(Tri-*n*-propylstannyl)-*N*-phenyl-*N*-benzoylhydroxylamine, Ie,** was similarly prepared as a golden viscous oil from bis(tripropyltin) oxide (2.56 g, 5.0 mmol) and the hydroxylamine (2.13 g, 10.0 mmol). The compound could not be distilled *in vacuo* but decomposed at temperatures in excess of *ca.* 150°. *Anal.* Calcd for $C_{22}H_{31}NO_2Sn$: C, 57.4; H, 6.8; N, 3.1. Found: C, 58.0; H, 6.5; N, 3.0.

4. **O-(Triphenylstannyl)-*N*-phenyl-*N*-benzoylhydroxylamine, If,** was obtained from triphenyltin hydroxide (3.67 g, 10.0 mmol) and the hydroxylamine (2.13 g, 10.0 mmol) and recrystallized from benzene as colorless needle crystals, mp 115.5–116.5°. *Anal.* Calcd for $C_{31}H_{25}NO_2Sn$: C, 66.2; H, 4.5; N, 2.5 (mol wt 562). Found: C, 65.9; H, 4.7; N, 2.4 (mol wt 561 (0.013 *M*)).

5. **O-(Triphenyllead)-*N*-phenyl-*N*-benzoylhydroxylamine, II.** Triphenyllead hydroxide (4.55 g, 10.0 mmol) and the hydroxylamine (2.13 g, 10.0 mmol) were azeotropically dehydrated in boiling benzene (50 ml). Removal of the solvent *in vacuo* gave a golden viscous oil, which could be recrystallized as an oil from hexane. Pumping at high vacuum for 24 hr produced a golden yellow crystalline solid, mp 44–46°. *Anal.* Calcd for $C_{31}H_{25}NO_2Pb$: C, 57.2; H, 3.9; N, 2.2. Found: C, 57.3; H, 4.0; N, 2.2.

6. **O-(Trimethylsilyl)-*N*-phenyl-*N*-benzoylhydroxylamine, IV.** *N*-Phenyl-*N*-benzoylhydroxylamine (2.13 g, 10.0 mmol) and hexamethyldisilazane (0.80 g, 5.0 mmol) were refluxed in dry tetrahydrofuran (50 ml) until the evolution of ammonia had stopped (1 hr). The solvent was removed and distillation of the residue yielded the *compound* as a golden oil, bp 108° (0.05 mm). *Anal.* Calcd for $C_{16}H_{19}NO_2Si$: C, 67.1; H, 6.6; N, 4.9. Found: C, 66.7; H, 6.5; N, 5.1.

7. **O-(Trimethylstannyl)-*N*-benzoylhydroxylamine, Ib.** Trimethyltin hydroxide (1.81 g, 10.0 mmol) and *N*-benzoylhydroxylamine (1.37 g, 10.0 mmol) were azeotropically dehydrated in boiling benzene. On cooling, the hot solution yielded **O-(trimethylstannyl)-*N*-benzoylhydroxylamine** as a white powder, mp 255° dec. The compound decomposed on attempted sublimation at 160° (0.01 mm). *Anal.* Calcd for $C_{10}H_{15}NO_2Sn$: C, 40.0; H, 5.0; N, 4.7 (mol wt 299). Found: C, 40.7; H, 5.0; N, 4.7 (mol wt 394 (0.015 *M*)). Nmr data (CH_2Cl_2 solution): τ 9.62 (*Me*$_3$Sn), $^2J(^{117,119}Sn-^1H)$ = 54.3, 56.7 Hz. Recrystallization from triethylamine yielded $(NEt_3H^+)(Me_2\overline{SnONCPhO}^-)$, mp ~200° dec. *Anal.* Calcd for $C_{16}H_{30}N_2O_2Sn$: C, 47.9; H, 7.5; N, 7.0. Found: C, 48.4; H, 7.2; N, 6.8.

8. **O-(Tri-*n*-propylstannyl)-*N*-benzoylhydroxylamine, Ic,** was similarly obtained by the azeotropic dehydration of the hydroxylamine (1.37 g, 10.0 mmol) and bis(tripropyltin) oxide (2.56 g, 5.0 mmol). The compound was a colorless viscous oil which could not be purified by distillation. *Anal.* Calcd for $C_{16}H_{27}NO_2Sn$: C, 50.0; H, 7.1; N, 3.7. Found: C, 49.5; H, 6.5; N, 2.8.

9. **Attempted Syntheses of O-(Triphenylstannyl)-*N*-benzoylhydroxylamine.** (a) Triphenyltin hydroxide (3.67 g, 10.0 mmol) and *N*-benzoylhydroxylamine (1.37 g, 10.0 mmol) were azeotropically dehydrated in benzene (50 ml). On cooling the hot mixture, a mass of white needle crystals were obtained, which were identified as tetraphenyltin by comparison with a authentic sample.

(b) An exothermic reaction took place when triethylamine (6.1 g, 60.0 mmol) was added to triphenyltin chloride (3.85 g, 10.0 mmol) and *N*-benzoylhydroxylamine (1.37 g, 10.0 mmol) in methanol (150 ml). After *ca.* 2 hr much solid had crystallized out of solution and was filtered off and dried; mp *ca.* 200° dec. *Anal.* Calcd for $C_{31}H_{36}N_2O_2Sn$: C, 63.4; H, 6.2; N, 4.8. Found: C, 63.1; H, 5.9; N, 4.7.

Registry No. *O*-(Trimethylstannyl)-*N,N*-diethylhydroxylamine, 37127-23-4; trimethyltin hydroxide, 56-24-6; *N,N*-diethylhydroxylamine, 3710-84-7; *O*-(trimethylstannyl)-*N*-phenyl-*N*-benzoylhydroxylamine, 39531-79-8; *N*-phenyl-*N*-benzoylhydroxylamine, 304-88-1; *O*-(tri-*n*-propylstannyl)-*N*-phenyl-*N*-benzoylhydroxylamine, 39046-68-9; bis(tripropyltin) oxide, 1067-29-4; *O*-(triphenylstannyl)-*N*-phenyl-*N*-benzoylhydroxylamine, 39046-69-0; triphenyltin hydroxide, 76-87-9; *O*-(triphenyllead)-*N*-phenyl-*N*-benzoylhydroxylamine, 39532-11-1; *O*-(trimethylsilyl)-*N*-phenyl-*N*-benzoylhydroxylamine, 39531-82-3; triphenyllead hydroxide, 894-08-6; hexamethyldisilazane, 999-97-3; *O*-(trimethylstannyl)-*N*-benzoylhydroxylamine, 39531-72-1; *N*-benzoylhydroxylamine, 495-18-1; *O*-(tri-*n*-propylstannyl)-*N*-benzoylhydroxylamine, 39531-73-2.

[13] P. G. Harrison, B. C. Lane, and J. J. Zuckerman, *Inorg. Chem.*, 11, 1537 (1972).

[14] D. B. Chambers, F. Glockling, and M. Weston, *J. Chem. Soc. A*, 1759 (1967).