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Preliminary communication

Organotin derivatives of substituted hydroxylamines

P.G. HARRISON
Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD (Great Britain)

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O-Trialkylstannyl oximes have been synthesized by several routes. All are monomeric except *O*-trimethylcyclohexanone oxime, which is apparently associated via distannoxane ring formation (1). *O*-Stannyl derivatives of *N*-substituted hydroxylamines are conveniently obtained in high yield by the azeotropic dehydration of the hydroxylamine (II) and the triorganotin oxide (hydroxide) (I).

$$\underset{(I)}{R_3SnOH} + \underset{(II)}{HONR^1R^2} \longrightarrow \underset{(III)}{R_3SnONR^1R^2} + H_2O \qquad (1)$$

(a, $R = Me$, $R^1 = R^2 = Et$;
b, $R = Me$, $R^1 = Ph$, $R^2 = \cdot CO \cdot Ph$;
c, $R = n\text{-}Pr$, $R^1 = Ph$, $R^2 = \cdot CO \cdot Ph$;
d, $R = Ph$, $R^1 = Ph$, $R^2 = \cdot CO \cdot Ph$;
e, $R = Me$, $R^1 = H$, $R^2 = \cdot CO \cdot Ph$;
f, $R = n\text{-}Pr$, $R^1 = H$, $R^2 = \cdot CO \cdot Ph$.)

O-Trimethylstannyl-*N*,*N*-diethylhydroxylamine (IIIa) is an essentially monomeric (mass spectrum) volatile liquid, which readily reverts to the protic compounds in air. The *O*-triorganotin derivatives of *N*-phenyl-*N*-benzoylhydroxylamine (PBHAH), on the other hand, are moisture stable, crystalline solids (the tripropyl derivative is an undistillable oil) which are monomeric in benzene (osmometry). The infrared carbonyl stretching frequencies of the solids are lowered by ca. 75 cm^{-1} (63 cm^{-1} for $Pr_3SnBPHA$) from that in free BPHAH, and are raised only slightly in solution, suggesting intramolecular coordination via the carbonyl oxygen to give a *cis*-R_3X_2Sn configuration. The mass spectra (recorded at 70 eV) exhibit, in addition to the parent molecular ion and other monotin-containing species of lower mass, several strong fragments of high mass which contain two tin atoms. High resolution mass measurements on the more abundant ditin fragments show that they possess the SnOSn backbone. Apparently the SnO—Sn

TABLE 1

PHYSICAL DATA FOR THE ORGANOTIN HYDROXYLAMINE DERIVATIVES

	Compound	*M.P. (b.p.)*	*Infrared data*[a]		*Tin-119m Mössbauer data*			
			ν(C=O)(cm^{-1})	*ν(N–O)(cm^{-1})*	*δ(mm/sec)*	*Δ(mm/sec)*	*Γ_1(mm/sec)*	*Γ_2(mm/sec)*
IIIa	$Me_3Sn-O-NEt_2$[b]	(30–32°/0.02mm)	–	912	1.40	1.98	1.26	1.22
IIIb	$Me_3Sn-O-NPh\cdot CO\cdot Ph$[c]	120–122°	1547	945, 938	1.34	2.36	1.39	1.36
IIIc	$n\text{-}Pr_3Sn-O-NPh\cdot CO\cdot Ph$	golden oil	1557	946	1.50	2.65	0.98	1.01
IIId	$Ph_3Sn-O-NPh\cdot CO\cdot Ph$	115.5–116.5	1540	940	1.26	1.94	0.92	0.92
IIIe	$Me_3Sn-O-NH\cdot CO\cdot Ph$[d]	255 (dec.)	1608, 1567, 1543	918	1.37	2.74	1.55	1.55
Vb	$NEt_3H^+\ Ph_3\overset{-}{Sn}-O-N\cdot CO\cdot Ph^-$	ca. 200 (dec.)	1605, 1570, 1543	918	1.23	1.74	1.81	1.88

[a] Nujol/halocarbon mull.

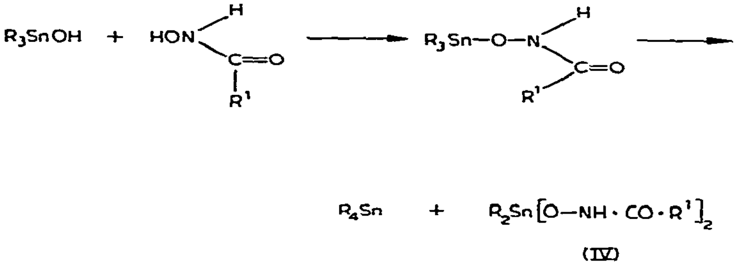
[b] NMR data: (CH_2Cl_2 solution) τ 9.68 (Me_3Sn), $J(^{117,119}Sn-^1H)$ 55.5 Hz (unresolved); triplet τ 8.97, quartet τ 7.42 (N–Et)J(H–H) ca. 7 Hz.

[c] NMR data: (CH_2Cl_2 solution) τ 9.58 (Me_3Sn), $J(^{117,119}Sn-^1H)$ 54.1, 56.7 Hz.

[d] NMR data: (CH_2Cl_2 solution) τ 9.62 (Me_3Sn), $J(^{117,119}Sn-^1H)$ 54.3, 56.7 Hz.

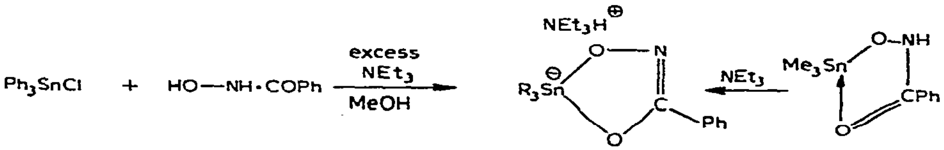
intermolecular distance in the BPHA derivatives, although essentially monomeric, is small enough to allow fission to give distannoxane fragments.

O-Trimethyl- and tripropylstannyl-*N*-benzoylhydroxylamine are generally similar, with additional intermolecular hydrogen bonding (illustrated by infrared dilution studies). The tripropyl derivative, however, a colourless oil when freshly prepared, over a period of 3—4 days deposits a white solid, which elemental analysis has shown to be the dipropyltin derivative (IV, R = n-Pr; R^1 = Ph). Attempts to prepare *O*-triphenylstannyl-*N*-benzoyl- and *O*-trimethylstannyl-*N*-acetyl-hydroxylamine resulted in similar disproportionations, and tetraphenyltin and the dimethyltin derivative (IV, R = Me, R^1 =·CO·Me) and tetramethyltin, respectively, were isolated in high yields.



(2)

Treatment of IIIe with triethylamine yields the cyclic organotin anion (Va), whilst the triphenyl analogue (Vb) is formed from the tin chloride, *N*-benzoylhydroxylamine and excess triethylamine in methanol.



(3)

(Va R = Me;
Vb R = Ph)

The tin-119m Mössbauer data (recorded at 77 K *vs.* a Ba^{119} ^{m}SnO$_3$ source) and other physical data for representative derivatives are gathered in Table 1. The composition of all derivatives was confirmed by microanalysis.

ACKNOWLEDGEMENT

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REFERENCE

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