Derivatives of Divalent Germanium, Tin, and Lead. Part I. The Protolysis of Cyclopentadienyltin(II) Compounds by Hydroxy-derivatives. Tin(II) Oximes and Hydroxylamines [1]

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Tin(II) dimethoxide, tin(II) diacetate, and the tin(II) derivatives of oximes and hydroxylamines are prepared by the protolysis of the tin(II)–carbon bonds of cyclopentadienyltin(II) compounds, and the tin-119*m* Mössbauer data reported. The structures of tin(II)–oxygen bonded compounds are discussed. Two main classes appear to exist: (i) those with strong intermolecular association, high thermal stability, and insolubility, which have isomer shifts in the range 2·91—3·13 mm s^{-1}, and (ii) those which exhibit solubility in organic solvents, and are only weakly associated, which have isomer shifts in excess of 3·15 mm s^{-1}, usually in the range 3·20—3·40 mm s^{-1}. Tin(II) cyanide and some tin(II)–nitrogen bonded compounds are prepared similarly. With cyclopentadienyltricarbonyltungsten hydride, a rapid autopolymerisation takes place forming a tin(IV)–tungsten bonded oligomer.

IN sharp contrast to organotin(IV) chemistry, where a large number of tin–oxygen bonded derivatives of organic protic reagents have been characterised, very few similar tin(II) compounds are known.[2] In the lower oxidation state, general synthetic procedures exist only for derivatives of inorganic and carboxylic acids, and the complex ions derived therefrom.[2] A few tin(II)

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[1] For a preliminary account of this work see P. G. Harrison, *J.C.S. Chem. Comm.*, 1972, 544.

[2] J. D. Donaldson, *Progr. Inorg. Chem.*, 1967, **8**, 287.

derivatives of alcohols,[3-5] phenols,[5-9] and silanols [10,11] have been prepared, but the routes used were either specific or of low yield. The esterification of anhydrous or hydrated stannous oxide by monofunctional alcohols and phenols has been used to prepare the tin(II) analogues of di- and oligo-stannoxanes.[7] Similar oligostannoxanes have been prepared from tin(II) acetate.[7] Here we describe a ready versatile synthesis of tin(II) derivatives of organic hydroxy-compounds, and in particular tin(II) oximes and hydroxylamines.

DISCUSSION

Dicyclopentadienyltin(II) and its methylcyclopentadienyl analogue have been shown to undergo ready oxidative hydrolysis in air.[12] This hydrolytic instability of the tin(II)–carbon bond indicates that these reagents may be suitable precursors for the synthesis of novel families of tin(II) derivatives, a rôle which organotin amines occupy in the higher oxidation state. This hypothesis is substantiated by the ready synthesis of the previously characterised tin(II) dimethoxide [4,5] and tin(II) acetate [13] from 2 mol of the protic reagent and the diorganotin(II) reagent in anhydrous benzene [equation (1)].

$$\mathrm{Sn^{II}(OMe)_2} \xleftarrow{\mathrm{2MeOH}} \mathrm{R_2Sn^{II}} \xrightarrow{\mathrm{2MeCO_2H}} \mathrm{Sn[O{\cdot}COMe]_2} \quad (1)$$

Although covalent organotin(IV) oximes [14,15] and hydroxylamine derivatives [16] are known, analogous tin(II) compounds are as yet uncharacterised. However, oximes have been shown to complex with stannous ions in dilute hydrochloric acid.[17] Bis(oximato)- and

Physical data for the tin(II) derivatives

Compound	Solvent and conditions	Appearance	Analysis (%) Found C	H	N	Calc. C	H	N	ν(C:N)/cm^{-1}	ν(N·O)/cm^{-1}	δ/mm s^{-1} [g,h]	Δ/mm s^{-1} [g,i]	Γ_1/mm s^{-1}	Γ_2/mm s^{-1}
(I) $\mathrm{Sn(O{\cdot}N{:}CHMe)_2}$	THF, exothermic	White crystals	18·7	3·1	10·8	19·1	3·2	11·2	1602s	935vs 960vs	3·22	2·26	1·27	1·22
(II) $\mathrm{Sn(O{\cdot}N{:}CMe_2)_2}$	THF, 3 h	White crystals	27·4	4·4	10·3	27·4	4·4	10·7	1614w 1635w	915vs	3·27	2·09	1·26	1·23
(III) $\mathrm{Sn(O{\cdot}N{:}CHPh)_2}$	THF, exothermic	White crystals	46·9	3·6	7·3	46·8	3·4	7·8	1588w	931vs 942vs	3·23	2·14	0·98	1·02
(IV) $\mathrm{Sn(O{\cdot}N{:}CPh_2)_2}$	THF, immediate	White solid	60·1	3·7	5·2	61·1	3·9	5·5	1595vvw	900m 942m	3·30	2·27	1·12	1·14
(V) $\mathrm{Sn[O{\cdot}N{:}C(Me)Ac]_2}$	THF, crystall'n on concentration	Pale yellow solid	30·4	3·7	8·2	30·1	3·8	8·8	1605w	905m [a] 915m	3·23	1·95	1·02	0·94
(VI) $\mathrm{Sn{\cdot}O{\cdot}N{:}CMe{\cdot}CMe{:}N{\cdot}O}$	THF, 12 h	Golden yellow crystals	20·5	2·9	11·4	20·6	2·6	12·0	1581m	900m 946s	3·30	1·90	1·39	1·08
(VII) $\mathrm{Sn{\cdot}O{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}O}$	THF, immediate	Pale yellow solid	33·2	2·3	5·2	33·1	2·0	5·5	1595m	914m	3·70	2·17	1·43	1·28
(VIII) $\mathrm{Sn[O{\cdot}N(Ph)Bz]_2}$	THF, exothermic crystall'n on concentration	Off-white solid	57·3	3·7	4·8	57·5	3·7	5·2		905m [b] 920s 926s	3·23	2·09	1·08	1·04
(IX) $\mathrm{Sn(O{\cdot}NHBz)_2}$	THF, exothermic crystall'n on concentration	White crystals	42·3	3·0	7·3	43·0	3·1	7·2		912 [c]	3·37	1·95	1·12	1·09
(X) $\mathrm{Sn(OMe)_2}$	THF, exothermic	White solid	13·1	3·3		13·3	3·4			1025vs [d]	3·02	1·97		
(XI) $\mathrm{Sn(O{\cdot}COMe)_2}$ [e]	THF, 5 min	White crystals	20·7	2·8		20·3	2·6				3·31 [22]	1·77		
(XII) $\mathrm{Sn(CN)_2}$	THF, immediate	White solid	13·6	0·1	16·0	14·1	0·0	16·4	2168m 2179m		3·28	2·23	1·70	1·61
(XIII) $\mathrm{Sn(imidazole)_2}$	THF, immediate	White solid	28·9	2·7	20·6	28·3	2·4	22·0			3·09	2·02		
(XIV) $\mathrm{Sn(1,2,4\text{-}triazole)_2}$	THF, immediate	White solid	18·6	1·3	30·1	18·3	1·5	32·0			3·60	2·14		
(XV) $\mathrm{Sn(N_2C_3Me_3)_2}$	Benzene, crystall'n on concentration	White crystals	42·7	5·6	16·3	42·7	5·4	16·6						
XVI) $\mathrm{[Sn\{W(CO)_3(\pi\text{-}C_5H_5)\}_2]_n}$	THF, exothermic	Vermilion crystals	24·9	1·7		24·5	1·3				2·08	2·05	1·51	0·83
SnO											2·91 [29]			
Tin(II)–oxygen heterocycles											2·95—3·13 [21]	1·76—1·98		
$\mathrm{Sn_3(PO_4)_2}$											3·05 [21]	1·90		
$\mathrm{Sn_3(AsO_4)_2}$											2·97 [21]	2·03		
Tin(II) carboxylates											3·15—3·48 [22,k]	1·56—1·89		

[a] ν(C=O): 1670m cm^{-1}. [b] ν(C=O): 1520vs,br cm^{-1}. [c] ν(C=O): 1597vs, 1586s, 1570s, 1549vs, 1528vs cm^{-1}; ν(N–H): 3200v,br cm^{-1}. [d] ν(C–O); ν(Sn–O): 570vs cm^{-1}. [e] Sublimes *ca.* 140° (bath)/0·05 mm. [f] ν(C=N). [g] Recorded at 77 K *vs.* a $\mathrm{BaSn^{119m}O_3}$ source. [h] Considered accurate to at least ±0·05 mm s^{-1}. [i] Considered accurate to at least ±0·01 mm s^{-1}. [j] Full width at half-height. [k] $\mathrm{Sn(O{\cdot}CO{\cdot}CH_2F)_2}$ has δ = 3·10 mm s^{-1} at 77 K and δ = 3·17 mm s^{-1} at room temperature.

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[3] H. Meerwein and E. Geschke, *J. prakt. Chem.*, 1936, **147**, 203.

[4] E. Amberger and M. Kula, *Ber.*, 1963, **96**, 2562.

[5] J. S. Morrison and H. M. Haendler, *J. Inorg. Nuclear Chem.*, 1967, **29**, 393.

[6] G. T. Cocks and J. J. Zuckerman, *Inorg. Chem.*, 1965, **4**, 592.

[7] D. E. Fenton, R. R. Gould, P. G. Harrison, T. B. Harvey, III, G. M. Omietanski, K. C.-T. Sze, and J. J. Zuckerman, *Inorg. Chim. Acta*, 1970, **4**, 235.

[8] J. J. Zuckerman, *J. Chem. Soc.*, 1963, 1322.

[9] H. J. Emeléus and J. J. Zuckerman, *J. Organometallic Chem.*, 1964, **1**, 328.

[10] F. A. Henglein, R. Lang, and L. Schmack, *Makromol. Chem.*, 1957, **22**, 103.

[11] R. Okawara, D. G. White, K. Fujitani, and H. Sato, *J. Amer. Chem. Soc.*, 1961, **83**, 1342.

[12] P. G. Harrison and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1969, **91**, 6885.

[13] J. D. Donaldson, W. Moser, and W. B. Simpson, *J. Chem. Soc.* (Suppl.), 1964, 5942.

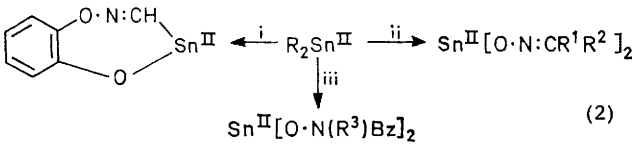
[14] P. G. Harrison and J. J. Zuckerman, *Inorg. Nuclear Chem. Letters*, 1970, **7**, 5.

[15] P. G. Harrison and J. J. Zuckerman, *Inorg. Chem.*, 1970, **9**, 175.

[16] P. G. Harrison, *J. Organometallic Chem.*, 1972, **38**, C5.

[17] V. M. Peshkova, E. S. Gur'eva, and L. M. Toldova, *Zhur. Neorg. Khim.*, 1968, **13**, 2896.

bis(hydroxylamino)-tin(II) compounds are readily prepared as generally air-sensitive solids (Table) *via* the protolysis of the diorganotin(II) reagents by the parent oxime or hydroxylamine, usually in anhydrous benzene or tetrahydrofuran [equation (2)]. Yields are generally in excess of 90%.



(2)

i, o-HO·C_6H_4·CH:N·OH; ii, 2(HO·N:CR^1R^2); iii, 2[HO·N(R^3)Bz]

Corroboration of the preservation of the lower oxidation state is given by the tin-119*m* isomer shifts (Table), which are all in excess of that of β-tin (2·65 mm s^{-1}), the generally accepted dividing line between the two valence states.[18]

From their physical properties, tin(II)–oxygen bonded compounds may be divided into two types. Strongly associated polymeric materials of high thermal stability and insolubility with a layer structure similar to that already established for stannous oxide,[19] in which each tin atom is bonded to four oxygen atoms; examples are tin(II) oxide itself, tin(II) arsenate, phosphate, and dimethoxide, and several tin(II)–oxygen heterocycles. These compounds all exhibit isomer shifts characteristically in the range 2·91—3·13 mm s^{-1}.[20,21] Tin(II) carboxylates,[22] siloxides,[23] oximes, and hydroxylamines, which exhibit varying degrees of solubility in organic solvents * † and appear to have a structure composed of discrete molecules with only weak intermolecular association in the solid. These gave isomer shifts in excess of 3·15 mm s^{-1} and frequently in the range 3·20—3·40 mm s^{-1}.[21-23] In the present case, the tin(II) oximes, including the heterocycle derived from dimethylglyoxime (VI) have isomer shifts in the range 3·22—3·30 mm s^{-1}. The heterocycle derived from salicylaldoxime (VII) has a significantly higher isomer shift of 3·70 mm s^{-1}, rationalised on the basis of the greater electron withdrawal of the phenoxide moiety. The hydroxylamine derivative (IX) has an isomer shift somewhat higher than the corresponding phenyl compound (VIII), but both are of the same order as for the oxime derivatives. All the compounds have quadrupole splittings in the range 1·77—2·20 mm s^{-1}. The origin of the quadrupole splitting in tin(II) compounds is the subject of debate. Covalent and point-charge models have been used, but neither is able to predict adequately the magnitude or sign of this quantity.[24]

Significant i.r. bands are listed in the Table. The C=N stretching vibration occurs as a weak band in the range 1581—1635 cm^{-1}, somewhat lower than in the corresponding monomeric triorganotin oximes (1625—1630 cm^{-1}).[15] The N–O stretching vibration may be identified usually as a strong band in the region 900—960 cm^{-1} both in the oxime and hydroxylamine derivatives. The carbonyl stretching vibration in the latter derivatives are lowered significantly from that in the free hydroxylamines, diagnostic of strong co-ordination of the acyl oxygen to tin, as in the similar triorganotin(IV) derivatives.[16,25] In contrast, the same vibration in the diacetylmonoxime derivative (V) is unchanged from the parent oxime. The tin–oxygen stretching frequency is not generally readily assignable. In tin(II) dimethoxide, however, it appears as an intense band at 560 cm^{-1}, in good agreement with the literature.[5]

Although most pseudohalide derivatives of tin(II) are known, one notable exception appears to be the cyanide. It is, however, immediately precipitated as a white air-sensitive solid on addition of hydrogen cyanide to a THF solution of di(methylcyclopentadienyl)tin(II). [equation (3)]. The observation of two bands at

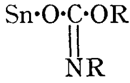
$$(MeC_5H_4)_2Sn^{II} + 2HCN \longrightarrow Sn^{II}(CN)_2 \qquad (3)$$

2168 and 2179 cm^{-1}, readily assigned to the C≡N stretching vibration, is consistent with a bent (C_{2v}) geometry for the molecule. The Mössbauer parameters are very similar to those for the oxime derivatives.

Tin(II) alkoxides add to the multiple bonds of isocyanates to form adducts which, by analogy with previous work have been assigned the tin–nitrogen bonded structure (A). However, the evidence for this formulation is not equivocal and the alternative structure (B) may not be ruled out.[7] Tin(II) phthalocyanine, for which structural confirmation of the lower oxidation state is available, is the sole previous example of a tin(II)–nitrogen bonded compound[26]. In the present case, although no cleavage of the cyclopentadienyltin(II) bonds by primary or secondary amines could be detected under the mild conditions used, 'active' nitrogen reagents reacted readily. Thus the tin(II) derivatives of imidazole (XIII), 1,2,4-triazole (XIV), and 3,4,5-trimethyl-1,2-diazole (XV) were obtained in almost quantitative yield. Whereas the compound (XV), when freshly prepared, is freely soluble in aprotic organic solvents, (XIII) and

Sn·NR·CO·OR′

(A)



$$\mathrm{Sn{\cdot}O{\cdot}\underset{\underset{NR}{\|}}{C}{\cdot}OR'}$$

(B)

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* Bis(triphenylsiloxy)tin(II) is essentially monomeric in benzene solution (P. G. Harrison, unpublished work).

† The ability of tin(II) acetate to sublime *in vacuo* is reasonable evidence for the discrete nature of this compound in the vapour phase.

[18] J. J. Zuckerman, 'Mössbauer Effect Methodology,' ed. I. J. Gruverman, Plenum Press, New York, 1967, vol. III, p. 15.

[19] W. J. Moore and L. Pauling, *J. Amer. Chem. Soc.*, 1941, **63**, 1392.

[20] A. J. Bearden, H. S. Marsh, and J. J. Zuckerman, *Inorg. Chem.*, 1966, **5**, 1260.

[21] J. K. Lees and P. A. Flinn, *J. Chem. Phys.*, 1968, **48**, 882.

[22] J. D. Donaldson and A. Jelen, *J. Chem. Soc.* (*A*), 1968, 1448.

[23] P. G. Harrison, *J.C.S., Chem. Comm.*, 1972, 544.

[24] J. D. Donaldson, E. J. Filmore, and M. J. Tricker, *J. Chem. Soc.* (*A*), 1971, 1109.

[25] P. G. Harrison and T. J. King, *J.C.S., Chem. Comm.*, 1972, 815.

[26] M. K. Friedel, B. F. Hoskins, R. L. Martin, and S. A. Mason, *Chem. Comm.*, 1970, 400.

(XIV) are insoluble, and presumably have structures involving bridging 1,3-azole rings similar to that postulated for the analogous trialkyltin imidazoles and triazoles,[27] thereby achieving co-ordination saturation at tin. With the 1,2-diazole derivative (XV) such intermolecular association is prevented by the proximity of the two nitrogen atoms. Surprisingly, the Mössbauer isomer shift of the triazole derivative (3·60 mm s^{-1}) is considerably greater than that of the imidazole derivative (3·09 mm s^{-1}) reflecting increased *s* electron character at the tin nucleus and an increased contribution of the ionic canonical form [$Sn^{2+}2(ring)^-$] in the character of the bonding of the former compound.

All the derivatives, except for $Sn(N_2C_3Me_3)_2$ which, like dicyclopentadienyltin(II),[12] polymerises during a period of hours to a brown, insoluble material shown by Mössbauer spectroscopy to be a metal–metal bonded tin(IV) polymer, show no tendency to autopolymerise in sealed tubes under nitrogen. On exposure to air, however, an oxidative hydrolysis takes place with the simultaneous appearance of a tin(IV) resonance in the range 0·13—0·36 mm s^{-1} of the Mössbauer spectrum. Not unexpectedly the process takes place less readily as the bulkiness of the organic residue increases.

The tin–transition metal derivatives so far characterised all contain tin in its higher oxidation state, whether originating as stannous or stannic tin.[28] The air-stable vermilion solid obtained from the exothermic reaction between di(methylcyclopentadienyl)tin(II) and cyclopentadienyltricarbonyltungsten hydride in tetrahydrofuran has Mössbauer parameters $\delta = 2{\cdot}08$ mm s^{-1}, $\Delta = 2{\cdot}05$ mm s^{-1}, well within the range for tin(IV) derivatives. Since the initial reaction product must involve tin(II)–tungsten bonds, a rapid auto-polymerisation or -oligomerisation must occur [equation (4)].

$$(MeC_5H_4)_2Sn^{II} + 2(\pi\text{-}C_5H_5)(CO)_3WH \longrightarrow \{Sn^{II}[W(CO)_3(\pi\text{-}C_5H_5)]_2\} \longrightarrow \frac{1}{n}\{Sn^{IV}[W(CO)_3(\pi\text{-}C_5H_5)]_2\}_n \qquad (4)$$

In the i.r. spectrum of the solid the product exhibits two groups of carbonyl stretching frequencies at 2012w,sh, 2004m, 1982s, 1968s and 1913s,sh, 1894vs, 1880s,sh, and 1866m. In dichloromethane solution, these are transferred into six bands, again in two groups 2015m, 2005m, 1979m, 1948m, 1922s, and 1905m,sh. In both the solid phase and in solution, the lower frequency bands are appreciably broader, than those in the higher frequency group.

EXPERIMENTAL

All manipulations were performed under an atmosphere of dry nitrogen or argon. All solvents were rigorously dried before use: tetrahydrofuran by sodium wire and thence distillation from lithium aluminium hydride, benzene by distillation from sodium wire and benzophenone. Dicyclopentadienyltin(II) and dimethylcyclopentadienyltin(II) were prepared from the organolithium reagent and anhydrous stannous chloride and THF or dimethoxyethane.

I.r. measurements were carried out using a Perkin-Elmer 521 instrument. Tin-119*m* Mössbauer measurements were made by the P.C.M.U. (Harwell) at 77 K *vs.* a $BaSn^{119m}O_3$ source. Calibration of the instrument was made using sodium nitroprusside. Least squares gave parameters which are considered accurate to at least ±0·05 mm s^{-1} (δ) and ±0·10 mm s^{-1} (Δ and Γ).

The syntheses of the compounds were very similar. Reaction conditions are given in the Table. Generally the protic reagent (0·002 mol) in anhydrous THF or benzene (5—10 ml) was added to dicyclopentadienyltin(II) or dimethylcyclopentadienyltin(II) (0·001 mol) in the same solvent (5—10 ml). The product was either precipitated immediately, over a short period, or on concentration of the solution.

Bis(cyclopentadienyltricarbonyltungsten)tin(IV).— Cyclopentadienyltricarbonyltungsten hydride (freshly sublimed (1·28 g, 0·79 mmol) in dry THF (5 ml) was added dropwise to dimethylcyclopentadienyltin(II) also in THF (5 ml). A very exothermic reaction took place and a dark brown solution was produced. The volume was reduced by about half, and dry pentane (5 ml) was added; a brown solid crystallised out. Extraction with dichloromethane, followed by rapid evaporation (the compound appears to deteriorate over a period of several hours in dichloromethane solution) gave the *compound* as a vermilion microcrystalline solid (Found: C, 24·9; H, 1·7%. Calc. for $C_{16}H_{10}O_6SnW_2$: C, 24·5; H, 1·3%).

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[27] M. J. Janssen, J. G. A. Luijten, and G. J. M. Van Der Kerk, *J. Organometallic Chem.*, 1964, **1**, 286.

[28] D. E. Fenton and J. J. Zuckerman, *Inorg. Chem.*, 1969, **8**, 1771.

[29] J. D. Donaldson and B. J. Senior, *J. Chem. Soc. (A)*, 1966, 1796.