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Synthesis and Reactions of some Triorganotin(IV) Esters of Arsenous Acid

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Abstract

Tris(triorganostannyl) arsenites, $(R_3SnO)_3As$ ($R = Pr^n, Bu^n, Ph$) and triorganostannyl alkylene arsenites, $R_3SnO\overline{AsOGO}$ [$R = Pr^n, Bu^n$, Ph and $G = -CH_2CH_2-, -CH(CH_3)CH_2-, -CH(CH_3)(CH_3)CH-, -CH(CH_3)CH_2CH_2-, -C(CH_3)_2(CH_3)_2C-, -C(CH_3)_2CH_2(CH_3)CH-$] have been obtained for the first time as white solids or colourless viscous liquids by the condensation of bis(triorganotin) oxide with aresenous oxide and 2,2′-oxybis-1,3,2-dioxarsolanes and -arsenanes, respectively. While the latter are volatile under reduced pressure, the former disproportionate on heating into bis(triorganotin) oxides and triorganostannyl metarsenite. All these monomeric hydrolysable compounds have been characterised by elemental analysis, IR and NMR (^1H, ^{13}C, ^{119}Sn) spectral data. The latter are consistent with configurational stability of the heterocyclic rings. A few cleavage and insertion reactions of these compounds have also been carried out to compare the reactivity of As–O and Sn–O linkages.

Introduction

Organosilyl esters of phosphorus [1, 2] and arsenic [3–5] oxy acids have been investigated in detail as a part of studies concerned with metallosiloxane monomers and polymers and many of these have found industrial applications. Only in recent years, has the interest been directed to the corresponding organostannyl esters. Organostannyl phosphates [6, 7] are structurally interesting polymeric species useful as polymerisation catalysts [8] and as wood preservatives [9]. Synthetic and structural studies of organostannyl arsinates [10–12] have also been reported. Organostannyl esters of arsenous acid, however, are still unknown.

The present communication deals with the synthesis, spectroscopic properties and reactions of some triorganotin arsenites containing Sn–O–As(III) linkage.

Experimental

All glass apparatus fitted with interchangeable standard ground joints were used and precautions were taken to exclude moisture. 2,2′-Oxybis-1,3,2-dioxarsolanes and -arsenanes [5, 13], triphenyltin isopropoxide [14] and arsenous acetate [15] were synthesised by the methods described previously.

Arsenic was determined [16] iodimetrically after decomposing the sample in boiling sodium hydroxide solution. Tin was estimated as tin oxide. Chlorine was estimated volumetrically by Volhard's method.

Infrared spectra were recorded as Nujol mulls or neat liquids using CsI pellets on a Perkin-Elmer spectrophotometer model 577 in the range 4000–200 cm^{-1}. ^1H and ^{119}Sn NMR spectra were recorded in CCl_4 solution using TMS and tetramethyltin as external references on a Jeol FX 90Q spectrometer. Molecular weights were determined by the cryoscopic method in freezing benzene.

Synthesis of Tris(tri-n-propylstannyl) Arsenite (1)

A mixture of bis(tri-n-propyltin) oxide (4.68 g) and arsenic trioxide (0.60 g) was heated for ~3 h at 120–125 °C. Arsenic trioxide dissolved slowly to give a light yellow viscous liquid (5.21 g). *Anal.* Found: As, 8.62; Sn, 41.32. Calc. for $C_{27}H_{63}AsO_3Sn_3$: As, 866; Sn, 41.14%.

Synthesis of Tris(tri-n-butylstannyl) Arsenite (2)

A mixture of bis(tri-n-butyltin) oxide (10.37 g) and arsenic trioxide (1.15 g) was heated for ~5 h at 120–125 °C. Arsenic trioxide dissolved slowly to give a light yellow viscous liquid (11.29 g). *Anal.* Found: As, 7.53; Sn, 36.08. Calc. for $C_{36}H_{81}AsO_3Sn_3$: As, 7.56; Sn, 35.88%. The above (6.48 g), on attempted distillation under reduced pressure, yielded bis(tris-n-butyltin) oxide (4.13 g) as a distillable fraction at 190–195 °C/0.3 mm (Found: Sn, 39.86; calc. for $C_{24}H_{54}OSn_2$: Sn, 39.73%) and a non-volatile residue (2.08 g).

Synthesis of Tris(triphenylstannyl) Arsenite (3)

(a) A mixture of triphenyltin hydroxide (6.67 g) and arsenic trioxide (0.60 g) in toluene (~40 ml) was refluxed under a Dean–Stark apparatus. Arsenic trioxide remained insoluble even after 30 h.

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TABLE I. Synthetic and Analytical Data for Triorganostannyl Alkylene Arsenites

Reactants (g)		Molar ratio	Product[a]	Compound number	Boiling point °C/mm (melting point) Yield (%)	% Analysis Found (Calc.)		Molecular weight Found (Calc.)
Triorganotin oxide or hydroxide	$(\overline{OGOAs})O$ G=					As	Sn	
$(Pr_3Sn)_2O$ 11.41	$-CH_2CH_2-$ 6.38	1:1	$Pr_3SnOAsOCH_2CH_2O$	**4**	112/0.2 97	18.83 (18.81)	29.93 (29.76)	399 (398)
$(Pr_3Sn)_2O$ 4.38	$-CH(CH_3)CH_2-$ 2.69	1:1	$Pr_3SnOAsOCH(CH_3)CH_2O$	**5**	102/0.01 97	18.05 (18.17)	28.84 (28.76)	398 (413)
$(Pr_3Sn)_2O$ 2.22	$CH(CH_3)(CH_3)CH-$ 1.48	1:1	$Pr_3SnOAsOCH(CH_3)(CH_3)CHO$	**6**	108/0.05 91	17.60 (17.57)	28.12 (27.80)	
$(Pr_3Sn)_2O$ 3.90	$-C(CH_3)_2(CH_3)_2C-$ 3.04	1:1	$Pr_3SnOAsOC(CH_3)_2(CH_3)_2CO$	**7**	112/0.1 95	16.46 (16.49)	26.29 (26.09)	
$(Pr_3Sn)_2O$ 4.93	$-CH(CH_3)CH_2CH_2-$ 3.30	1:1	$Pr_3SnOAsOCH(CH_3)CH_2CH_2O$	**8**	121/0.3 91	17.52 (17.57)	27.96 (27.80)	
$(Pr_3Sn)_2O$ 2.44	$-C(CH_3)_2CH_2(CH_3)CH-$ 1.90	1:1	$Pr_3SnOAsOC(CH_3)_2CH_2(CH_3)CHO$	**9**	105/0.05 86	16.42 (16.49)	26.17 (26.09)	
$(Bu_3Sn)_2O$ 7.82	$-CH_2CH_2-$ 3.76	1:1	$Bu_3SnOAsOCH_2CH_2O$	**10**	123/0.05 93	17.08 (17.02)	27.16 (26.93)	456 (411)
$(Bu_3Sn)_2O$ 5.55	$-CH(CH_3)CH_2-$ 2.93	1:1	$Bu_3SnOAsOCH(CH_3)CH_2O$	**11**	134/0.05 94	16.53 (16.49)	26.14 (26.10)	
$(Bu_3Sn)_2O$ 7.22	$-CH(CH_3)(CH_3)CH-$ 4.15	1:1	$Bu_3SnOAsOCH(CH_3)(CH_3)CHO$	**12**	130/0.3 92	15.88 (16.00)	25.47 (25.32)	
$(Bu_3Sn)_2O$ 3.60	$-C(CH_3)_2(CH_3)_2C-$ 2.40	1:1	$Bu_3SnOAsOC(CH_3)_2(CH_3)_2CO$	**13**	142/0.5 96	15.01 (15.10)	24.09 (23.89)	
$(Bu_3Sn)_2O$ 4.66	$-CH(CH_3)CH_2CH_2-$ 2.68	1:1	$Bu_3SnOAsOCH(CH_3)CH_2CH_2O$	**14**	133/0.2 96	15.80 (16.00)	25.42 (25.32)	
$(Bu_3Sn)_2O$ 5.60	$-C(CH_3)_2CH_2(CH_3)CH-$ 3.72	1:1	$Bu_3SnOAsO(CH_3)_2CH_2(CH_3)CHO$	**15**	145/0.1 95	14.99 (15.10)	24.03 (23.89)	
Ph_3SnOH 8.71	$-CH_2CH_2-$ 3.40	2:1	$Ph_3SnOAsOCH_2CH_2O$	**16**	(110) 98	14.86 (14.98)	23.75 (23.70)	491 (501)
Ph_3SnOH 5.14	$-CH(CH_3)CH_2-$ 2.20	2:1	$Ph_3SnOAsOCH(CH_3)CH_2O$	**17**	(70) 97	14.55 (14.57)	23.13 (23.06)	
Ph_3SnOH 2.05	$-C(CH_3)_2(CH_3)_2C-$ 1.10	2:1	$Ph_3SnOAsOC(CH_3)_2(CH_3)_2CO$	**18**	– 98	13.49 (13.47)	21.38 (21.32)	
Ph_3SnOH 4.36	$-CH(CH_3)CH_2CH_2-$ 2.20	2:1	$Ph_3SnOAsOCH(CH_3)CH_2CH_2O$	**19**	(79) 96	13.94 (14.18)	22.55 (22.45)	
Ph_3SnOH 2.97	$-C(CH_3)_2CH_2(CH_3)CH-$ 1.61	2:1	$Ph_3SnOAsOC(CH_3)_2CH_2(CH_3)CHO$	**20**	(81) 98	13.44 (13.47)	2140 (21.32)	

[a] All compounds are colourless viscous liquids except compounds **13**, **14**, **16** and **17** which are white solids.

(b) A mixture of triphenyltin isopropoxide (2.39 g) and arsenous acetate (0.49 g) in a 3:1 molar ratio in toluene (~60 ml) was refluxed under column. The isopropyl acetate liberated in the reaction was distilled out slowly in ~8 h. On removal of the solvent under reduced pressure, a white foamy solid (2.19 g, 95% yield, melting point (m.p.) 109 °C) was obtained. *Anal.* Found: As, 6.42; Sn, 30.51. Calc. for $C_{54}H_{45}AsO_3Sn_3$: As, 6.40; Sn, 30.38%.

Synthesis of Triorganostannyl Alkylene Arsenites

(a) Reaction between bis(tri-n-butyltin) oxide and 2,2′-oxybis-1,3,2-dioxarsolane in 1:1 molar ratio

A mixture of bis(tri-n-butyltin) oxide (7.82 g) and 2,2′-oxybis-1,3,2-dioxarsolane (3.76 g) was refluxed in benzene (~30 ml) for ~2 h. The solvent was removed and the residue was distilled under reduced pressure to give a colourless viscous liquid (10.77 g, 93%).

The above procedure was adopted for the synthesis of various title compounds. Synthetic and analytical data are summarised in Table I.

(b) Reaction between triphenyltin hydroxide and 2,2′-oxybis-1,3,2-dioxarsolane in 2:1 molar ratio

A mixture of 2,2′-oxybis-1,3,2-dioxarsolane (3.40 g) and triphenyltin hydroxide (8.71 g) in benzene (~40 ml) was refluxed under a Dean–Stark apparatus till the dehydration was complete. The solvent was removed under reduced pressure to yield 2-triphenyl stannoxy-1,3,2-dioxarsolane as a white powder.

Other triphenylstannoxy derivatives were prepared by the same method and the pertinent data are given in Table I.

(c) Reaction between phenylisothiocyanate and 2-tributylstannoxy-4,4,5,5-tetramethyl-1,3,2-dioxarsolane in 1:1 molar ratio

A mixture of phenylisothiocyanate (0.86 g) and 2-tributylstannoxy-4,4,5,5-tetramethyl-1,3,2-dioxarsolane (3.16 g) was heated at 110–130 °C and the mixture was periodically checked by IR spectroscopy for the disappearance of the strong peak at ~2200 cm^{-1}. The reaction was completed after ~15 h yielding the adduct as a brown viscous liquid (3.98 g).

Other reactions between Sn–O–As bonded compounds and phenylisocyanate or isothiocyanate were carried out similarly (by heating the reaction mixture at 110–130 °C) and the time required for completion of reaction is indicated below

The products in all the above reactions analysed reasonably well for the expected adducts.

(d) Reaction between 2-triphenylstannoxy-3-methyl-1,3,2-dioxarsolane and thionyl chloride in 1:1 molar ratio

To the benzene (~30 ml) solution of 2-triphenylstannoxy-3-methyl-1,3,2-dioxarsolane (4.25 g) was added thionyl chloride (0.98 g) in benzene and the contents were refluxed for ~2 h. The solvent was removed under reduced pressure yielding a heterogeneous residue. 2-Chloro-3-methyl-1,3,2-dioxarsolane (1.42 g) was extracted from the residue with n-hexane and distilled (1.05 g), boiling point (b.p.) 62 °C/5 mm. *Anal.* Found: As, 40.56; Cl, 19.17. Calc. for $C_3H_6AsClO_2$: As, 40.66; Cl, 19.22%. Triphenyltin chloride (2.98 g) was left as a white solid (m.p. 106 °C) insoluble in n-hexane.

(e) Reaction between 2-triphenylstannoxy-tetramethyl-1,3,2-dioxarsolane and diisopropylphosphorochloridate in 1:1 molar ratio

A mixture of 2-triphenylstannoxy-tetramethyl-1,3,2-dioxarsolane (5.08 g) and diisopropylphosphoro chloridate (2.03 g) in benzene was refluxed for ~6 h. The solvent was removed *in vacuo* yielding a semisolid residue (7.05 g). Fractional distillation of the above yielded 2-(diisopropylphosphato)-4,4,5,5-tetramethyl-1,3,2-dioxarsolane as a colourless viscous liquid (2.74 g, 86% yield, b.p. 88–90 °C/0.4 mm) leaving behind triphenyltin chloride as a white solid (3.62 g, m.p. 105 °C). *Anal.* Found: As, 23.66. Calc. for $C_8H_{18}AsO_6P$: As, 23.73%.

(f) Reaction between 2-triphenylstannoxy-3-methyl-1,3,2-dioxarsonane and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaboralane in 1:1 molar ratio

A mixture of 2-triphenylstannoxy-3-methyl-1,3,2-dioxarsenane (1.19 g) and 2-chlorotetramethyl-1,3,2-dioxaboralene (0.47 g) was refluxed in benzene (~30 ml) for ~6 h. The solvent was distilled out and the residue was dried under reduced pressure yielding a whitish semisolid (1.96 g). The boroxyarsolane (0.78 g, 86% yield) was obtained as a colourless viscous liquid by extraction of the above residue with n-hexane. *Anal.* Found: As, 24.98. Calc. for $C_{10}H_{19}AsBO_5$: As, 24.52%. Triphenyltin chloride was left behind as a white solid (1.09 g, m.p. 107 °C).

Reactants			Molar ratio	Time (h)
$Bu_3SnO\overline{AsOC(CH_3)_2(CH_3)_2CO}$	+	PhNCO	1:1	5
$(Bu_3SnO)_3As$	+	PhNCO	1:1	6
$(Bu_3SnO)_3As$	+	PhNCO	1:2	11
$(Bu_3SnO)_3As$	+	PhNCO	1:3	Incomplete after 18 h
$(Bu_3SnO)_3As$	+	PhNCS	1:1	12
$(Bu_3SnO)_3As$	+	PhNCS	1:2	16
$(Bu_3SnO)_3As$	+	PhNCS	1:3	Incomplete after 24 h

TABLE II. ^{13}C NMR Spectral Data for Trialkylstannyl Arsenites

Compound	Chemical shifts (δ ppm) of tin alkyl carbons				$^{119}Sn-^{13}C$ Coupling constants (Hz)		
	C_1	C_2	C_3	C_4	^1J	^2J	^3J
$[(C_4H_9{}^n)_3SnO]_3As$	16.52	28.17	27.14	13.65	368.60	18.31	63.48
$(C_4H_9{}^n)_3SnO\overline{AsOCMe_2CMe_2O}{}^a$	16.41	27.79	26.92	13.65	364.34	21.97	–
$[(C_3H_7{}^n)_3SnO]_3As$	19.17	19.28	18.63	–	368.60	19.52	57.38
$(C_3H_7{}^n)_3SnO\overline{AsOCH_2CHMeO}{}^b$	19.82	19.23	18.63	–	364.94	–	63.48

[a] Other peaks: 83.48, 25.89 (broadened). [b] Other peaks: 74.97, 72.97, 72.64, 71.67, 19.07.

Results and Discussion

Tris(trialkylstannyl) arsenites have been obtained in quantitative yield by the condensation of bis(trialkyltin) oxide with arsenous oxide in 3:1 molar ratio.

$$3(R_3Sn)_2O + As_2O_3 \longrightarrow 2(R_3SnO)_3As$$

$R = Bu^n, Pr^n$

Attemps to prepare tris(triphenylstannyl) arsenite by the above route were unsuccessful. However, it could be obtained in quantitative yield by the condensation of triphenyltin isopropoxide with arsenous acetate in 3:1 molar ratio in refluxing toluene

$$Ph_3SnOPr^i + As(OCOCH_3)_3 \longrightarrow (Ph_3SnO)_3As + Pr^iOCOCH_3\uparrow$$

Tris(triphenylstannyl) arsenite is a white solid (m.p. 109 °C) whereas the tripropyl and tributylstannyl derivatives are non-volatile light-yellow viscous liquids, which disproportionate at 150–200 °C/0.1 mm to give bis(trialkyltin) oxide as a volatile fraction and a semisolid residue. The mode of disproportionation appears to proceed as below

$$(R_3SnO)_3As \longrightarrow (R_3Sn)_2O + (R_3SnOAsO)_n$$

The molecular weight of the polymeric residue could not be determined.

The IR spectra of tris(triorganostannyl) arsenites show a close resemblance with those of the corresponding bis(triorganotin) oxides except for the disappearance of the broad and strong ν(Sn–O–Sn) peak [17] at ~780 cm^{-1} and the appearance of a sharp peak of strong intensity at 715 ± 10 cm^{-1} which could be assigned to As–O Sn. The ^{119}Sn NMR spectra show chemical shift values of +71.6, +72.8 and −126.5 for the tripropyl, tributyl and triphenyl tin derivatives, respectively. These values are quite close to the corresponding values for the bis(triorganotin) oxides [18] and indicate the tetra coordinate nature of the tin atom. The tetra coordination of tin is further confirmed by the ^{13}C NMR spectral data (Table II) of these compounds in which ^1J(C–Sn) value of 368.6 Hz has been observed for trialkyltin derivatives [19].

The mixed cyclic esters of arsenous acid, triorganostannyl alkylene arsenites, (named as 2-triorganostannoxy-1,3,2-dioxarsolanes and -arsenanes) are readily obtained as thermally stable compounds by the following routes

$$(R_3Sn)_2O + (\overline{OGOAs})_2O \longrightarrow 2R_3SnO\overline{AsOGO}$$

$R = Pr^n, Bu^n$

$$2Ph_3SnOH + (\overline{OGOAs})_2O \longrightarrow 2Ph_3SnO\overline{AsOGO} + H_2O\uparrow$$

G = $-CH_2CH_2-$, $-CH(CH_3)CH_2-$, $-CH(CH_3)(CH_3)CH-$, $-CH(CH_3)CH_2CH_2-$, $-C(CH_3)_2(CH_3)_2C-$ and $-C(CH_3)_2-CH_2(CH_3)CH-$.

The former codisproportionation reactions are very facile and are completed in refluxing benzene while in the latter route, the triphenylstannoxy derivatives are obtained by the azeotropic removal of liberated water with benzene. The trialkyltin derivatives are volatile colourless viscous liquids; the triphenyltin derivatives, on the other hand, are sharp melting white solids except the tetramethyl-1,3,2-dioxarsolane derivative which is a colourless viscous liquid (Table I). All these compounds are highly soluble in common organic solvents like benzene, toluene, acetone, chloroform and carbon tetrachloride.

Triorganostannyl alkylene arsenites are susceptible towards moisture and are completely hydrolysed by water to form the glycol and organotin oxide or hydroxide along with the precipitation of arsenous oxide.

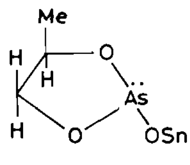
Triorganostannyl alkylene arsenites have been characterised by their IR and NMR (^1H, ^{119}Sn and ^{13}C) spectral data. Although the IR spectra are quite complicated, the relevant peaks (e.g. Sn–O–As, C–O(As), As–O(C) and Sn–C) could be recognised on the basis of earlier reports [17, 20–23] and their positions are given in Table III. Due to the lack of suitable data in the 300–200 cm^{-1} [24] region,

TABLE III. Some Relevant Infrared and ^{119}Sn NMR Spectral Data for Triorganostannyl Arsenites

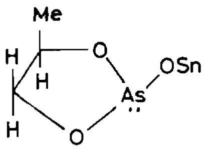
Compound number	ν(As)OC	νSnOAs	νAsO(C)	νas Sn–C	νs Sn–C	^{119}Sn NMR spectral data	
						Solvent	Chemical shifts (ppm)
1	–	710s	–	590m	510w	CCl_4	+71.62
2	–	720s	–	600m	515s	CCl_4	+72.79
3	–	705s	–	–	–	C_6H_6	–126.47
4	1025s	795s	635s	600m	515s	–	–
5	1020s	800s	665s	610m	530w	CCl_4	+90.53
6	1055s	705s	665s	630s	530w	–	–
7	1145s	725s	655s	600m	515m	neat	+94.04
8	1080s	775s	645s	580m	540w	CCl_4	+92.40
9	1150s	700m	655s	600m	540m	–	–
10	1025s	800s	630s	600w	530m	–	–
11	1015s	795s	660s	605m	510m	neat	+90.60
12	1060s	795s	665s	600w	540w	neat	+93.71
13	1145s	720s	660s	640m	520s	neat	+92.90
14	1100s	725s	670s	610s	530w	–	–
15	1130m	795s	670s	610w	525w	CCl_4	+95.44
16	1020s	775s	620m	–	–	C_6H_6	–99.63
17	1065s	770s	620m	–	–	CCl_4	–98.95
18	1150s	780s	630m	–	–	CCl_4	–100.60
19	1070s	765s	645m	–	–	CCl_4	–99.28
20	1150s	800s	630s	–	–	–	–

s = strong, m = medium, w = weak.

ν(Sn–C) in triphenyltin compounds could not be assigned. The PMR spectra are of second order and have not been fully analysed. In trialkylstannyl derivatives, there are further complications due to the overlapping of peaks in the region δ 0.5–2.0 ppm. All the spectra are, however, consistent with the preposed structure (as indicated by the relative peak areas) and, like triphenylsilyl alkylene arsenites [5], show configurational stability of the ring. Thus, the spectra of all the three triorganostannyl ethylene arsenites give a multiplet centred at 3.60 ppm corresponding to AA′BB′ coupling. In the corresponding triphenylstannyl tetramethylethylene arsenite, two signals of equal intensity are present at 1.20 and 1.36 ppm, thus indicating the non-equivalence of the methyl groups present as *cis* and *trans* to the triphenylstannoxy group. The two other 5-membered heterocycles, propylene and sym-dimethylethylene arsenites (derived from propane 1,2 and butane-2,3-diols) give spectra consistent with $ABCD_3$ and ABX_3Y_3 coupling. From integration of the methyl doublets (centred at 1.05 and 1.09 ppm) of triphenylstannylpropylene arsenite, the amounts of *trans* and *cis* isomers could be roughly estimated to be in 6:1 ratio.



Trans



Cis

The ^{119}Sn NMR chemical shift values for trialkylstannyl alkylene arsenites (Table III) are in the range +94 ± 4 ppm, thus showing a downfield shift of ~20 ppm and of ~10 ppm in comparison to the values for tris(trialkylstannyl) arsenites and bis(trialkylstannyl) oxides respectively [25]. The corresponding triphenylstannyl derivatives give a chemical shift of about –99 ppm which is about 20 ppm upfield from the value reported [26] for $(Ph_3Sn)_2O$ (–80.60 ppm in $CHCl_3$). The high field ^{119}Sn chemical shifts found for triphenyltin derivatives in general in comparison to the corresponding trialkyltin derivatives has been explained [27] on the basis of π-back bonding between the aromatic system and the vacant tin 5d orbitals [25]. The electron withdrawing effect of the alkylene arsenite moiety which is responsible for the downfield shift of the tin signal in trialkyltin derivatives, appears to enhance the backbonding in triphenyltin derivatives thereby making the tin atom more shielded. Surprisingly the tin atom in tris-(triphenylstannyl) arsenite, (showing a chemical shift of –126 ppm) is more shielded than in the heterocyclic compounds.

The ^{13}C NMR spectra (Table II) of only two compounds in this series (tributylstannyl tetramethylethylene arsenite and tripropylstannyl propylene arsenite) have been recorded. The ^{119}Sn–^{13}C coupling constants (^1J = 364 Hz) are in the same range as these for tris(trialkylstannyl) arsenites. The tin chemical shifts as well as tin–carbon coupling constants are consistent with 4-coordinate tin in all triorganostannyl arsenites. Thus, like triorganotin alkoxide, these compounds do not show any tendency for association [19].

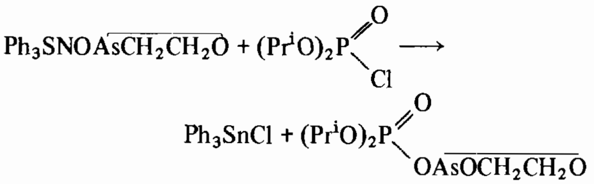
Reactions of the compounds of the type $R_3SnO\overline{AsOGO}$ with thionyl chloride in 1:1 molar ratios give the products of the following type by cleavage of the As–O–Sn linkage

$$Ph_3SnO\overline{AsOGO} + SOCl_2 \longrightarrow Ph_3SnCl + Cl\overline{AsOGO} + SO_2\uparrow$$

$G = -CH(CH_3)CH_2-,\ -C(CH_3)_2(CH_3)_2C-$

Cleavage of the exocyclic As–O bond indicates the higher reactivity of the As–O–Sn linkage in comparison to the As–O–C linkage.

The ready cleavage of the As–O–Sn linkage in stannoxy arsolanes and arsenanes is further shown by their reactions with diisopropylphosphoro chloridate and 2-chloro-tetramethyl-1,3,2-dioxaborolane

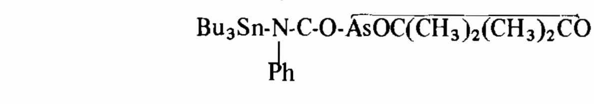


$$Ph_3SNO\overline{AsCH_2CH_2O} + (Pr^iO)_2P\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown Cl\end{smallmatrix} \longrightarrow Ph_3SnCl + (Pr^iO)_2P\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown O\overline{AsOCH_2CH_2O}\end{smallmatrix}$$

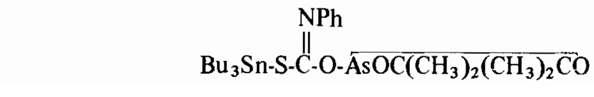
$$Ph_3SnO\overline{AsOCH(CH_3)CH_2CH_2O} + Cl\overline{BOC(CH_3)_2(CH_3)_2CO} \longrightarrow Ph_3SnCl + \overline{OC(CH_3)_2(CH_3)_2COB}O\overline{AsOCH(CH_3)CH_2CH_2O}$$

These reactions proceed with the transfer of chlorine to tin and that of the arsinoxy group to phosphorus or boron and demonstrate the synthetic utility of stannyl arsenites in the preparation of arsinoxy derivatives of other elements like phosphorus and boron. The products are readily separated either by fractional distillation or fractional dissolution in a suitable solvent.

The higher reactivity of the Sn–O linkage in comparison to the As–O linkage in Sn–O–As bonded compounds is further indicated by the preferential insertion of PhNCO and PhNCS in the former



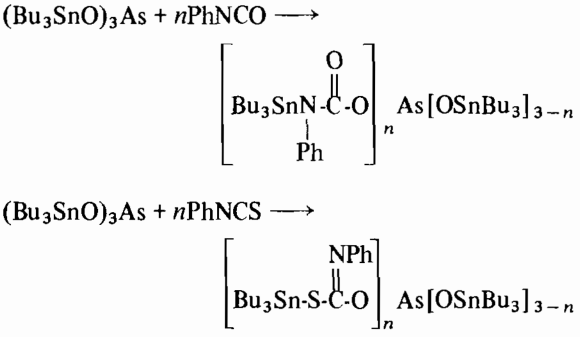
$$Bu_3SnO\overline{AsOC(CH_3)_2(CH_3)_2CO} + PhNCO \longrightarrow Bu_3Sn\text{-}\underset{Ph}{N}\text{-}C\text{-}O\text{-}\overline{AsOC(CH_3)_2(CH_3)_2CO}$$



$$Bu_3SnO\overline{AsOC(CH_3)_2(CH_3)_2CO} + PhNCS \longrightarrow Bu_3Sn\text{-}S\text{-}\overset{NPh}{\overset{\|}{C}}\text{-}O\text{-}\overline{AsOC(CH_3)_2(CH_3)_2CO}$$

The mode of insertion appears to be similar to those reported for organotin alkoxides [28]. However, in contrast to the facile insertion reactions of Sn–O–C bonded compounds, the above reactions appear to proceed only under forcing conditions (by heating the reaction mixture neat at 110–130 °C). The completion of reaction was checked by the disappearance of a strong peak at 2200 cm^{-1} (due to $\nu(N{=}C{=}O)$ and $\nu(N{=}C{=}S)$) in the product. The ^{119}Sn NMR spectra of isocyanate and isothiocyanate adducts show chemical shifts of 76.3 and 75.9 ppm respectively. These values are almost 20 ppm upfield from the starting material.

Tris(tributylstannyl) arsenite undergoes similar insertion reactions to yield 1:1 and 1:2 adducts, the latter being the final products even with excess of heterocumulene and heating of ~20 h.



$$(Bu_3SnO)_3As + nPhNCO \longrightarrow \left[Bu_3Sn\underset{Ph}{N}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\right]_n As[OSnBu_3]_{3-n}$$

$$(Bu_3SnO)_3As + nPhNCS \longrightarrow \left[Bu_3Sn\text{-}S\text{-}\overset{NPh}{\overset{\|}{C}}\text{-}O\right]_n As[OSnBu_3]_{3-n}$$

$n = 1,2$

All the above products are brownish viscous liquids susceptible to moisture; the phenylisocyanate derivatives showing a much enhanced sensitivity. This may be readily explained on the basis of reported differences in the hydrolytic behaviour of Sn–N and Sn–S bonded compounds [28]. Oxybisarsolanes and -arsenanes do not appear to react with phenylisocyanate and isothiocyanate even under forcing conditions.

Interestingly, both mono and bis adducts with PhNCO give only a single tin NMR signal at 68.04 and 67.06 ppm, respectively. Similarly the PhNCS adducts also show single tin signals, the position being 73.58 and 72.98 ppm, respectively. This could only be explained on the basis of fast exchange between oxygen and nitrogen and sulphur bonded organotin moieties. However, further investigations are needed on this interesting phenomenon.

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