

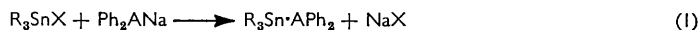
582. *Organometallic Compounds Containing Tin–Arsenic or Tin–Antimony Bonds.*

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Organometallic compounds of the type $R_3Sn \cdot APh_2$, with $R = Et, Pr^i$, or Bu^i , and $A = As$ or Sb , have been prepared and characterised. Fission of the Sn–As and Sn–Sb bonds occurred slowly upon reaction with methyl iodide, to give the trialkyltin iodide in each case, but the expected quaternary salt was isolated only in the case of the arsenic compounds. Oxidation of the stannylarsines gave the esters $R_3SnO \cdot As(O)Ph_2$ (prepared for comparison by another method), but the product from the oxidation of the stannylstibines could not be identified.

ORGANOMETALLIC compounds containing the tin–arsenic or tin–antimony bond were briefly described in 1936,¹ but details of their preparation were sparse. The compounds were said to be reducing agents and excellent antioxidant-additives for lubricating oils, but their physical and chemical properties were not presented. This Paper describes a synthetic route to these compounds, and recounts their simple physical properties and their mode of reaction with oxygen and with methyl iodide.

In the light of our earlier experience with the stannylphosphines,² we made initial attempts to prepare compounds containing Sn–As or Sn–Sb bonds by the process shown in equation (1)



where X was a halogen and A was either arsenic or antimony. The sodium derivatives were prepared from the tertiary arsine or stibine by reaction with sodium in liquid ammonia.³ Phenylsodium, necessarily produced at the same time in equimolar quantity, was eliminated from the reaction mixture by the addition of an equimolar proportion of ammonium bromide. If the phenylsodium was not eliminated in this way, it competed for the added trialkyltin chloride, and the yields of the stannyl–arsines and –stibines were correspondingly reduced. The method gave excellent yields of the stannylarsines and moderate yields of the stannyl–stibines.

The Sn–As and Sn–Sb bonds appear to have similar thermal stabilities to the Sn–P bonds in the analogous compounds,² since purification was achieved by fractional distillation under reduced pressure at about 250°. It seems reasonable to attribute this stability to a measure of π -bonding between the tin and arsenic (or antimony) atoms. Further indication of π -bonding in the Sn–As bond comes from the dipole moment of $Bu^i_3Sn \cdot AsPh_2$ (0.65 D), which is significantly less than that of the phosphorus analogue (0.96 D). This decrease may be rationalised on the assumption that there is more π -bonding in the Sn–As than in the Sn–P bond. Thus, while the Sn–As bond is slightly the longer, arsenic is slightly more electropositive than phosphorus, and these two factors should approximately cancel out. The lower moment of the Sn–As compound may therefore be accounted for by supposing that the p_π lone-pair of arsenic is associated more with tin than is the p_π lone-pair of phosphorus. This is not too surprising, since the tin atom uses vacant $5d$ orbitals for π -bonding, and overlap will obviously be more effective with $4p$ (for arsenic than with $3p$ (for phosphorus) orbitals.

Molecular-weight studies showed the compounds to be monomeric in benzene solution; dimerisation might have been expected had there been no π -bonding. The marked similarity to the Sn–P compounds was also reflected in the interaction of the Sn–As compounds with oxygen and with polar reagents such as methyl iodide, although the reactions were much slower than those of the stannylphosphines. For instance, quantitative fission of

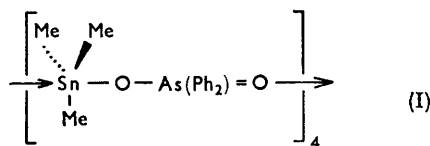
¹ Standard Oil Development Co., B.P. 445,813 (1936) (*Chem. Zentr.*, 1936, II, 1287).

² Campbell, Fowles, and Nixon, *J.*, 1964, 1389.

³ Hewertson and Watson, *J.*, 1962, 1490.

the Sn-As bond with methyl iodide occurred only after refluxing in diethyl ether, whereas methyl iodide reacted violently with the stannylphosphines at room temperature. The products, dimethyldiphenylarsonium iodide and trialkyltin iodide, were consistent with nucleophilic attack on the tin atom. Although the appropriate trialkyltin iodide was obtained from the reaction of methyl iodide with $R_3Sn \cdot SbPh_2$, the stibonium salt could not be isolated, no doubt because of the marked reluctance of arylstibines to form stibonium salts. Atmospheric oxidation at room temperature cleaves the Sn-As bond and simultaneously converts arsenic to the quinquevalent state, forming the trialkylstannyl diphenylarsinates $R_3SnO \cdot As(O)Ph_2$. These compounds were characterised by analysis and by comparison with compounds synthesised in good yield by condensation of diphenylarsinic acid with the required trialkyltin hydroxide or oxide. It is possible that the trialkylstannyl diphenylarsinite is formed as an intermediate and is rapidly oxidised to $R_3SnO \cdot As(O)Ph_2$ (cf. the analogous silicon compounds⁴). Although atmospheric oxidation of the stannylstibines gave a white sticky solid, attempts to isolate a specific oxidation product failed. Further, stannyl stibinates were not detected in the reaction mixtures of diphenylstibinic acid and trialkyltin oxides under varying conditions.

All the stannyl arsenates were found to be dimeric in dilute benzene solution, with the exception of the trimethylstannyl derivative which was tetrameric. Trimethylstannyl diphenylarsinate has a strong infrared band at 547 cm.^{-1} , which can be assigned to the Sn-C antisymmetric stretching frequency.⁵ The absence of a peak corresponding to the Sn-C symmetrical stretching frequency suggests a planar trimethylstannyl group, in accordance



with the structure (I). A single peak (at 543 cm.^{-1}) was also noted for the corresponding phosphorus compound. Spectroscopic evidence for the co-ordination of oxygen to tin ($\text{As}=\text{O} \longrightarrow \text{Sn}$) was unfortunately difficult to obtain, because of the complex nature of the spectrum in the region where one expects to find the $\text{As}=\text{O}$ stretching frequency.⁶

EXPERIMENTAL

Infrared spectra of solids were measured as Nujol mulls, using a Unicam S.P. 200 or an Infracord (KBr) spectrophotometer and are listed in Table 1. Molecular weights were measured ebullioscopically on benzene solutions, using a Gallenkamp Ebulliometer. Dipole moments were measured by the method previously described;² the moment of $\text{Bu}_3\text{Sn} \cdot \text{AsPh}_2$ was found to be 0.65 D.

Preparations.—The stannyl-arsines and -stibines were prepared on a vacuum-line, under strictly anhydrous conditions.

Diphenyl(trialkylstannyl)arsines. Triphenylarsine (3.0 g., 9.8 mmole) was weighed into a 100 ml. three-necked flask. Dry liquid ammonia (35 ml.) was condensed into the flask under a vacuum at -78° , and sodium (0.45 g., 19.6 mg.-atom) was added in small pieces. The initial blue colour was rapidly discharged as the contents of the flask were stirred, and a dark brown solution resulted. After addition of ammonium bromide (0.98 g., 10 mmoles) with vigorous stirring, the colour changed to orange-red. The required trialkyltin bromide (10 mmole) in dry ether (30 ml.) was added quickly, to prevent formation of the solid trialkyltin bromide ammoniate in the neck of the dropping-funnel. The mixture was stirred for 5 min., whereupon the orange-red colour was discharged with simultaneous separation of a cream precipitate. Evaporation (reduced pressure) of the solvents left a semi-solid mass which was extracted with dry ether and filtered under nitrogen. The cloudy, pale yellow liquid remaining after the evaporation of the ether was vacuum-distilled through a 4 in. Vigreux column.

⁴ Schmidbaur and Schmidt, *Angew. Chem.*, 1961, **73**, 655.

⁵ Beattie and McQuillan, *J.*, 1963, 1519.

⁶ Philips and Tyree, *J. Amer. Chem. Soc.*, 1961, **83**, 1806.

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TABLE 1.
Infrared spectra of trimethyltin iodide (A), diphenylarsinic acid (B),
and $R_3SnO\cdot As(O)Ph_2$ compounds.

A	B	$R_3SnO\cdot As(O)Ph_2$				Assignment	
		R = Me	R = Et	R = Bu ^a	R = Ph		
1410w *	1470s	1465s	1465s	1465s	1465s	Nujol band	
	1442s	1440s	1440s	1440s	1442s		
1200w *	1380s	1380s	1380s	1380s	1380s	Nujol band	
	1320w	1310w	1305w	1305w	1310w		
	1180w	1180w	1178w	1180w		As=O str.	
	1160w	1155w	1155w	1155w	1155w		
	1090s	1090s	1090s	1090s	1090s		
	1070w	1070w	1065w	1075w	1080w		
	1030w	1027w	1027w	1020w	1030w		
	1000w	1000w	1000w	1000w	1000w		
			965w	965w			
		930w	930w	925w			
		883m	885s	887m	895s		880sh
		850s	870s	860s	860s		850s
782s *	795s			798m		C-H deform.	
	778s	775s					
	750s			745s	743m		
722m *	740s	743s	740s	740s	730m		
	690s	690s	695s	695s	690s	C-H deform.	
	675w	685w	680s	680m	678m		
	670w	670w	670s	670m	670m	Sn-C antisym. str. Sn-C sym. str.	
542s † 513w †		547s					
	478s	483s				Sn-C antisym. str. Sn-C sym. str.	
	448s	465s					
331vs †							

* Nujol mull.³ † Benzene solution.²

TABLE 2.
Diphenyl(trialkylstannyl)-arsine and -stibines.

Compound	B. p.	Yield (%)	Formula	Required			<i>M</i>	Found			<i>M</i>
				C (%)	H (%)	Sn (%)		C (%)	H (%)	Sn (%)	
$Et_3Sn\cdot AsPh_2$	140—143/0.15 mm	61	$C_{18}H_{25}AsSn$	49.7	5.8	—	—	50.3	6.1	—	—
$Pr^i_3Sn\cdot AsPh_2$	159—161/0.20 mm	62	$C_{21}H_{31}AsSn$	52.9	6.6	—	—	52.9	7.1	—	—
$Bu^i_3Sn\cdot AsPh_2$	163—164/0.09 mm	60	$C_{24}H_{37}AsSn$	55.5	7.2	—	519	55.3	7.3	—	494
$Et_3Sn\cdot SbPh_2$	144—146/0.18 mm	27	$C_{18}H_{25}SbSn$	44.9	5.2	24.6	482	45.1	5.4	24.3	448
$Pr^i_3Sn\cdot SbPh_2$	168—170/0.13 mm	35	$C_{21}H_{31}SbSn$	48.1	6.0	22.7	—	48.3	6.2	23.1	—
$Bu^i_3Sn\cdot SbPh_2$	179—180/0.15 mm	26	$C_{24}H_{37}SbSn$	50.9	6.5	21.0	—	50.9	7.0	21.4	—

The yields, physical properties, and analytical data of the compounds are collected in Table 2. The omission of ammonium bromide resulted in considerably reduced yields of the stannylarsines.

Diphenyl(trialkylstannyl)stibines. These compounds were prepared from triphenylstibine (6.0 g., 17.0 mmole), sodium (0.78 g., 33.9 mg.-atom), ammonium bromide (1.67 g., 17 mmole), and the appropriate trialkyltin bromide (17 mmole), by a route similar to that described above. The yields, physical properties, and analytical data of these compounds are also listed in Table 2.

Fission of the Sn-As Bond.—(a) *Oxidation.* The diphenyl(trialkylstannyl)arsine (0.5 g.) was pipetted under nitrogen into a small conical flask connected to a closed system containing dry air. The pressure in the system gradually dropped, and after 24 hr. the trialkylstannyl diphenylarsinate was obtained as a sticky solid which was recrystallised from ethanol. The yields, physical properties, and analytical data are listed in Table 3.

(b) *Methyl iodide.* A mixture of diphenyl(tri-*n*-butylstannyl)arsine (0.3 g.), methyl iodide (1 ml.), and ether (2 ml.) was refluxed under nitrogen for 2 hr., whereupon a white precipitate

gradually separated. The solid was filtered and washed with ether to give dimethyldiphenylarsonium iodide (0.096 g., 44%), m. p. 208—209° (Found: C, 43.7; H, 4.4; As, 19.1. Calc. for $C_{14}H_{16}AsI$: C, 43.5; H, 4.2; As, 19.4%). From the filtrate, tri-*n*-butyltin iodide was isolated by way of the ammoniate (Found: Sn, 28.7. Calc. for Bu^n_3SnI : Sn, 28.5%). A similar reaction was found to take place between diphenyl(triethylstannyl)arsine and methyl iodide.

TABLE 3.
Trialkylstannyl diphenylarsinates, obtained by oxidation of the diphenyl(tri-alkylstannyl)arsines.

Compound	M. p.	Yield (%)	Formula	Required			Found		
				C (%)	H (%)	<i>M</i>	C (%)	H (%)	<i>M</i>
$Et_3SnO \cdot As(O)Ph_2$	220—223° *	54	$C_{18}H_{25}O_2AsSn$	46.3	5.4	—	46.2	5.8	—
$Pr^i_3Sn \cdot OAs(O)Ph_2$	204—205	51	$C_{21}H_{31}O_2AsSn$	49.5	6.1	509	49.4	6.2	1050
$Bu^i_3Sn \cdot OAs(O)Ph_2$	197—198	41	$C_{24}H_{37}O_2AsSn$	52.3	6.8	551	52.3	6.9	1152

* After repeated recrystallization, this arsenate melted at 220—223°, but consistently softened at 165—170°. If the sample was rapidly heated, it melted completely just below 170°.

Synthesis of Trialkyl (and triphenyl)stannyl Diphenylarsinates.—The appropriate trialkyltin oxide (5 mmoles) or hydroxide (10 mmoles) was added to a solution of diphenylarsinic acid (10 mmole) in benzene (150 ml.), and the mixture heated under reflux for 12 hr. In syntheses employing a trialkyltin hydroxide, any unreacted hydroxide was filtered off before concentration of the solution to about 25 ml. The solution was cooled and set aside overnight at room temperature, and a white precipitate was deposited. Crystallisation from ethanol gave the pure trialkylstannyl diphenylarsinate. Triphenylstannyl diphenylarsinate, which gradually separated as a fine white precipitate from the hot reaction mixture and could not be crystallised from the usual organic solvents, was purified by repeated washing with hot benzene and ethanol.

The yields, physical properties, and analytical data are listed in Table 4.

TABLE 4.
Trialkyl (and triphenyl)stannyl diphenylarsinates.

Compound	M. p.	Yield (%)	Formula	Required			Found		
				C (%)	H (%)	<i>M</i>	C (%)	H (%)	<i>M</i>
$Me_3SnO \cdot As(O)Ph_2$	207—208°	59	$C_{15}H_{19}O_2AsSn$	42.2	4.5	425	42.2	4.3	1606
$Et_3SnO \cdot As(O)Ph_2$	166—167	74	$C_{18}H_{25}O_2AsSn$	46.3	5.4	467	46.2	5.6	995
$Pr^i_3Sn \cdot OAs(O)Ph_2$	204—205	59	$C_{21}H_{31}O_2AsSn$	49.5	6.1	509	49.8	6.2	1050
$Bu^i_3Sn \cdot OAs(O)Ph_2$	196—197	54	$C_{24}H_{37}O_2AsSn$	52.3	6.8	—	52.3	7.0	—
$Ph_3SnO \cdot As(O)Ph_2$	323—324	90	$C_{30}H_{25}O_2AsSn$	59.0	4.1	—	59.2	4.0	—

Diphenylarsinic acid was prepared by oxidation of diphenylarsinosodium, obtained by cleavage of triphenylarsine with sodium in liquid ammonia. Sodium (0.75 g.) was added in small pieces to liquid ammonia (50 ml.) containing triphenylarsine (5 g.). When the original blue colour had changed to orange, ammonia was allowed to distil off, and the yellow residue was dissolved in ether (40 ml.). Air was slowly passed through the stirred solution until the colour was discharged and a white precipitate formed. Oxidation was completed by the slow addition of hydrogen peroxide (10 vol.; 10 ml.), and when water (30 ml.) was added, a clear solution resulted. Acidification caused precipitation of diphenylarsinic acid (2.67 g., 6.2%), m. p. 173°.

Fission of the Sn-Sb Bond.—(a) *Oxidation.* The diphenyl(tri-alkylstannyl)stibines were more sensitive to oxidation than the corresponding arsenic derivatives, but it proved impossible to isolate pure products from the reaction; oxidation appeared to have produced a polymeric species containing Sb-O-Sn bonds.

(b) *Methyl iodide.* When diphenyl(tri-*n*-butylstannyl)stibine was boiled under reflux with methyl iodide in ether for 90 min., tri-*n*-butylstannyl iodide was isolated in 59% yield. No quaternary salt of the antimony residue could be obtained.

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