79. *Preparation of Monomers and Polymers containing* Sn–O–As(V) *Linkages.*

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The compounds $[-SnMe_2{\cdot}O{\cdot}AsRO{\cdot}O-]_x$ (R = Me or Ph), $(SnPh_3{\cdot}O)_2AsPhO$, $(SnPh_3{\cdot}O)_3AsO$, $SnMe_2(O{\cdot}AsMe_2O)_2$, $[-O{\cdot}AsO{<}(O{\cdot}SnMe_2O)_2{>}AsO{\cdot}O{\cdot}SnMe_2-]_x$ and $SnMe_2(O{\cdot}AsPhO{\cdot}OH)_2$ have been prepared, three methods being involved. The properties of these products are discussed.

Interest has been shown recently in the preparation and properties of organometallosiloxanes, *i.e.*, compounds containing metals inserted into the –Si–O–Si–O– backbone of siloxanes. For instance, polymers and monomers of this type containing Si–O–As groups have been reported.[1] Since tin falls below silicon in Group IV of the Periodic Table and since silicon and tin(IV) have almost identical electronegativity values we have studied the preparation and properties of analogous compounds containing Sn–O–As linkages.

The only previous syntheses of such compounds involve: (*a*) interaction of alkyltin acetates with arylarsonic acids;[2] (*b*) reaction of alkyl- or aryl-tin oxides with alkyl- or aryl-arsonic acids;[2] and (*c*) interaction of dimethyltin dichloride with disodium arsenate.[3]

Our work involved three synthetic methods: (*a*) Reaction of the sodium or potassium salt of an arsenic-containing acid with alkyl- or aryl-tin chlorides, *viz.*:

$$xSnMe_2Cl_2 + xAsRO(ONa)_2 \longrightarrow 2xNaCl + [-SnMe_2{\cdot}O{\cdot}AsRO{\cdot}O-]_x \quad . \; . \; . \; . \quad (1, 2)$$

(1, R = Ph; 2, R = Me)

$$2SnPh_3Cl + AsPhO(ONa)_2 \longrightarrow 2NaCl + (SnPh_3{\cdot}O)_2AsPhO \quad . \; . \; . \; . \; . \; . \quad (3)$$

$$3SnPh_3Cl + 3KH_2AsO_4 \longrightarrow 3KCl + 2H_3AsO_4 + (SnPh_3{\cdot}O)_3AsO \quad . \; . \; . \; . \; . \quad (4)$$

(*b*) Reaction of the silver salt of an arsenic-containing acid with dimethyltin dichloride, *viz.*:

$$SnMe_2Cl_2 + 2AsMe_2O{\cdot}OAg \longrightarrow 2AgCl + SnMe_2(O{\cdot}AsMe_2O)_2 \quad . \; . \; . \; . \; . \; . \quad (5)$$

$$3xSnMe_2Cl_2 + 2xAg_3AsO_4 \longrightarrow 6xAgCl + [-O{\cdot}AsO{<}(O{\cdot}SnMe_2{\cdot}O)_2{>}AsO{\cdot}O{\cdot}SnMe_2-]_x \quad . \quad (6)$$

(*c*) Reaction of phenylarsonic acid with dimethyltin dichloride, *viz.*:

$$SnMe_2Cl_2 + 2AsPhO(OH)_2 \longrightarrow 2HCl + SnMe_2(O{\cdot}AsPhO{\cdot}OH)_2 \quad . \; . \; . \; . \; . \quad (7)$$

The same product is obtained in reaction (7) when an excess of dimethyltin dichloride is used. Only when the disodium salt of phenylarsonic acid is employed is the fully substituted derivative obtained (reaction 1).

It is of interest that the reaction analogous to (4), in which triphenylsilyl chloride[1c] was used instead of the tin compound, occurred in pure diethyl ether whereas the tin compound reacted only if a mixed aqueous solvent was used. Also, reactions analogous to (7), involving alkylsilicon halides,[1a] proceed in a non-polar solvent, but dimethyltin dichloride and phenylarsonic acid do not react in boiling benzene even in the presence of a

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[1] (*a*) Kary and Frisch, *J. Amer. Chem. Soc.*, 1957, **79**, 2140; (*b*) Schmidt and Schmidbaur, *Angew. Chem.*, 1959, **71**, 553; (*c*) Chamberland and MacDiarmid, *J. Amer. Chem. Soc.*, 1960, **82**, 4542.

[2] Walde, Van Essen, jun., and Zbornik, U.S.P. 2,762,821/1956; *Chem. Abs.*, 1957, **51**, 4424.

[3] Rochow, Seyforth, and Smith, jun., *J. Amer. Chem. Soc.*, 1953, **75**, 3099.

hydrohalogen acceptor such as pyridine, or in the molten state in the absence of solvent during 90 min. though in the presence of water a rapid reaction occurs.

Since substitution at a silicon atom, with a nucleophilic reagent, generally involves a quinquecovalent intermediate,[4] reaction of organosilicon chlorides with these arsenic compounds probably proceeds through the formation of an intermediate species of the type $\geqslant\mathrm{As{=}O{\rightarrow}\overset{|}{\underset{|}{Si}}Cl}$. If the 5*d*-orbitals of tin are less effective than the 3*d*-orbitals of silicon in forming complexes of this type, then the absence of reaction of the tin compounds under similar experimental conditions is understandable. However, in the presence of a highly polar solvent, such as water, ionisation of the $\geqslant\mathrm{Sn{-}Cl}$ linkage will be increased and consequently a reaction mechanism involving ionisation could become more important. The experimental results strongly suggest that the reactions studied proceed by an ionisation mechanism.

The Sn–O–As linkages in the triphenyltin derivatives possess considerable covalent character as indicated by the solubility of these compounds in benzene and by their fairly low melting points. The much smaller solubility in organic solvents and absence of true melting points for the dimethyltin derivatives suggest a higher ionic character in the Sn–O–As bonds. This is to be expected since two electronegative $\mathrm{{-}O{-}\overset{|}{\underset{|}{As}}{<}}$ groups attached to a tin atom will make the tin more positive—and hence the $\geqslant\mathrm{Sn{-}O{-}}$ linkages more ionic—than when only one is attached. In addition, cross-linking by $\geqslant\mathrm{As{=}O{\rightarrow}\overset{|}{\underset{|}{Sn}}{<}}$ bridges will be more favourable sterically in the dimethyltin compounds. The physical properties of the polymeric species will also be greatly affected by their degree of polymerisation.

It is evident that the Sn–O–As linkage is not extensively hydrolysed since the compounds are, in general, prepared in a medium containing large amounts of water. The solubility of certain of the compounds in aqueous acids and alkalis is probably due to the fact that in these reagents they are almost completely hydrolysed to soluble materials, *e.g.*:

$$[\mathrm{-O{\cdot}SnMe_2{\cdot}O{\cdot}AsPhO-}]_x + 2x\mathrm{H_3O^+} \longrightarrow x[\mathrm{SnMe_2(H_2O)_2}]^{2+} + x\mathrm{AsPhO(OH)_2}$$

$$[\mathrm{-O{\cdot}SnMe_2{\cdot}O{\cdot}AsPhO-}]_x + 2x\mathrm{OH^-} \longrightarrow x[\mathrm{SnMe_2O_2}]^{2-} + x\mathrm{AsPhO(OH)_2}$$

EXPERIMENTAL

Infrared Spectra.—A Perkin–Elmer model 21, double-beam recording spectrophotometer with a sodium chloride prism was used. All compounds were examined in KBr discs at concentrations of approximately 2—3 mg. per 300 mg. The absorption maxima of the compounds studied are tabulated and are correlated separately for monomeric and polymeric species.

Polymeric Dimethyltin Phenylarsonate.—Addition of dimethyltin dichloride (2·20 g., 10·0 mmoles) in methanol (30 ml.) to phenylarsonic acid (2·02 g., 10·0 mmoles), which had been previously neutralised with sodium hydroxide and diluted to 60 ml. with water, yielded a white precipitate which, after washing with water and methanol and drying *in vacuo*, consisted of a pure *polymer*, $[\mathrm{-O{\cdot}SnMe_2{\cdot}O{\cdot}AsPhO-}]_x$ (2·6 g., 75%), decomp. 455°, soluble in dilute acids and bases, slightly soluble in methanol and acetone, and insoluble in benzene, water, or ether (Found: C, 28·2; H, 3·3; As, 22·1. $\mathrm{C_8H_{11}AsO_3Sn}$ requires C, 27·5; H, 3·2; As, 21·5%).

The qualitative test for $\mathrm{SnMe_2}$ with dithizone reagent[5] was positive. In this test the deep green colour of solutions of diphenylthiocarbazone in buffered methanolic solution becomes reddish-orange on addition of a dialkyl- or triaryl-tin compound. Organoarsenic compounds do not interfere.

Polymeric Dimethyltin Methylarsonate.—Addition of dimethyltin dichloride (2·20 g., 10·0 mmoles) in water (60 ml.) to disodium methylarsonate (2·74 g., 10·0 mmoles) in water (40 ml.) yielded, after 20 min., a white gelatinous precipitate which after washing with water and methanol and drying *in vacuo* consisted of pure *polymer*, $[\mathrm{-O{\cdot}SnMe_2{\cdot}O{\cdot}AsMeO-}]_x$ (1·58 g., 55%), decomp. 400°, soluble in acids and bases, slightly soluble in methanol, and insoluble in acetone,

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[4] Eaborn, " Organosilicon Compounds," Butterworths Scientific Publications, London, 1960, p. 112.

[5] Aldridge and Cremer, *Analyst*, 1957, **82**, 37.

Infrared spectra (*cm.*$^{-1}$) *of* (*A*) $SnMe_2(O{\cdot}AsMe_2O)_2$, (*B*) $SnMe_2(O{\cdot}AsPhO{\cdot}OH)_2$, (*C*) $(SnPh_3{\cdot}O)_2AsPhO$, (*D*) $(SnPh_3{\cdot}O)_3AsO$, (*E*) $[–O{\cdot}SnMe_2{\cdot}O{\cdot}AsMeO–]_x$, (*F*) $[–O{\cdot}AsO<(O{\cdot}SnMe_2{\cdot}O)_2>AsO{\cdot}O{\cdot}SnMe_2–]_x$, and (*G*) $[–O{\cdot}SnMe_2{\cdot}O{\cdot}AsPhO–]_x$.

(*A*)	(*B*)	(*C*)	(*D*)	(*E*)	(*F*)	(*G*)
3425w	3425w	3410m	3425m	3420m	3390m	3390w
3020, 2940m	2899w	3060m	3025m	2930w	2925m	3020; 2910w
2330w	2330w	2340m				2325vw
	1980vw		1942vw			1960vw
1890; 1856vw			1888vw			1900vw
1669; 1619w	1620w	1628m	1628w			1820vw
			1576w	1629w	1628m	1620w
	1490; 1478w	1481m	1482m			1482w
1412m	1444m					1440m
		1430s	1430s		1406m	
	1310vw	1330w	1332w	1395m	1388m	
1256s						1308vw
1230w	1204w				1299m	
1175m	1158w	1178vw	1153vw	1265m		
	1092m	1091m		1184w	1190w	1180vw
		1077m	1075m		1147vw	
		1020w	1021m			1093m
	998w	997m	998m	885s		892vs
	913s			862vs	866vs	869vs
897vs	890s	885m	892s			818vs
842vs	858s	857vs	855s	756vs	766vs	762vs
	815m		832s			736m
		802s	800s			687m
	773vs		787s			
742vs	743m	723s	726vs			
	696m	693vs	693vs			
	685m	685m				

benzene, or water (Found: C, 12·9; H, 3·3; As, 26·9. $C_3H_9AsO_3Sn$ requires C, 12·6; H, 3·2; As, 26·1%). The dithizone test was positive.

Bistriphenyltin Phenylarsonate.—Addition of triphenyltin chloride (7·71 g., 20·0 mmoles) in methanol (60 ml.) to phenylarsonic acid (2·02 g., 10·0 mmoles) (previously neutralised with sodium hydroxide) in methanol (60 ml.) yielded a white precipitate which was removed by filtration after the solution had been heated to the b. p. The product obtained (7·73 g., 86%), after being washed with methanol and water and dried, melted at 245—247° and was soluble in benzene and acids, slightly soluble in acetone and methanol, and insoluble in water and bases (Found: C, 56·1; H, 4·0; As, 8·3. $C_{42}H_{35}AsO_3Sn_2$ requires C, 56·05; H, 3·9; As, 8·3%), giving a positive dithizone test.

Tristriphenyltin Arsenate.—Addition of triphenyltin chloride (3·85 g., 10·0 mmoles) in acetone (25 ml.) to potassium dihydrogen arsenate (1·80 g., 10·0 mmoles) in water (25 ml.) yielded in 48 hr. a dense oil mixed with a white solid. The mixed solvent was removed by decantation and the partly solid residue was treated with methanol to remove traces of potassium chloride and arsenic acid. In this treatment, the oil was converted into a white solid (2·34 g., 59%). This product, *tristriphenyltin arsenate*, melted at 227—230° and was soluble in benzene, slightly soluble in methanol and acetone, and insoluble in ether or water (Found: C, 54·35; H, 3·7; As, 6·6. $C_{54}H_{45}AsO_4Sn_3$ requires C, 54·5; H, 3·8; As, 6·3%), dithizone test positive.

After the above reagents had been stirred in ether at room temperature during 20 hr. they were recovered quantitatively.

Dimethyltin Cacodylate.—Addition of dimethyltin dichloride (1·10 g., 5·00 mmoles) in water (25 ml.) to silver cacodylate (2·45 g., 10·0 mmoles) in water (50 ml.) immediately precipitated silver chloride. The filtrate yielded plates of *dimethyltin cacodylate* (1·72 g., 82%) on slow evaporation. This product decomposed at 330°, was soluble in water and acids, slightly soluble in methanol, and insoluble in ether, acetone, or benzene (Found: C, 17·25; H, 4·2; As, 35·7. $C_6H_{18}As_2O_4Sn$ requires C, 17·05; H, 4·3; As, 35·45%), positive dithizone test.

Polymeric Dimethyltin Arsenate.—Addition of dimethyltin dichloride (6·60 g., 30·0 mmoles) in water (25 ml.) to silver orthoarsenate (9·56 g., 20·0 mmoles) yielded a grey precipitate. After 2 hours' refluxing and then filtration, the filtrate was evaporated to yield white flakes of pure *polymer* $[–O{\cdot}AsO<(O{\cdot}SnMe_2{\cdot}O)_2>AsO{\cdot}O{\cdot}SnMe_2–]_x$ (0·76 g.), decomp. 350°, insoluble in common organic solvents and only very slightly soluble in water (Found: C, 9·8; H, 2·6; As, 21·0. $C_6H_{18}As_2O_8Sn_3$ requires C, 9·95; H, 2·5; As, 20·7%), giving a positive dithizone test.

Dimethyltin Bisphenylarsonate.—Addition of phenylarsonic acid (1·01 g., 5·00 mmoles) in hot water (50 ml.) to dimethyltin dichloride (1·10 g., 5·00 mmoles), in water (25 ml.) yielded a white precipitate, which after being washed with water and dried *in vacuo*, consisted of the *bisphenylarsonate* (0·80 g., 46%), decomp. 380°, insoluble in water, acetone, ether, or benzene but dissolving in acid or base (Found: C, 30·5; H, 3·3; As, 26·9. $C_{14}H_{18}As_2O_6Sn$ requires C, 30·5; H, 3·3; As, 27·2%), giving a positive test with dithizone. The filtrate contained 99% of the chloride used, and 40% of the dimethyltin dichloride employed was recovered.

When phenylarsonic acid (4·04 g., 20·0 mmoles), in hot water (100 ml.) was added to dimethyltin dichloride (2·20 g., 10·0 mmoles) in water (25 ml.), a 73% yield was obtained (Found: C, 31·7; H, 3·4%).

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